



Origin, mineral speciation and geochemical baseline mapping of Ni and Cr in agricultural topsoils of Thiva Valley (central Greece)

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ABSTRACT

Lithogenic Ni and Cr enrichment in agricultural topsoils of Thiva Valley (central Greece) is the result of transport of weathered parent rock fragments from upslope ultramafic sources. Chemical and mineralogical evolution of these potentially toxic elements between the trace metal bearing bedrock and the overlying soil horizon along two weathering profiles located in an area where the ultramafic rocks are exposed was accomplished to unravel the source and mineral speciation dynamics of Ni and Cr in the soil system of Thiva Valley. Within the soil horizons, Ni primarily occurs in serpentine (average 0.5 wt.% of NiO) and secondary weathering products like smectites (average 0.5 wt.% of NiO) and goethite (average 1.1 wt.% of NiO). Significant amounts of this element are also hosted in less abundant Mn (hydr)oxides. On the contrary, Cr is mainly bounded with inherited chromite (average 54.7 wt.% of Cr₂O₃) and to a lesser extent with Cr-magnetite (average 12.2 wt.% of Cr₂O₃) and Cr silicates like enstatite (average 0.8 wt.% of Cr₂O₃). As a result of the solid speciation and the applied decomposition method (aqua regia digestion), the soil geochemical anomalies within the valley are more pronounced with respect to Ni (up to 2640 mg/kg) compared to Cr (up to 856 mg/kg). The geochemical baseline maps produced by the ordinary kriging interpolation method reveal a strong tendency for large Ni and Cr amounts in the southern part of the area warning about the potential occurrence of high metal values in soils of Thiva town with an approximate number of 25,000 exposed population. Based on the mineralogical residence of Ni and Cr differences in their potential bioavailability and leaching to groundwater are anticipated.

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1. Introduction

Igneous ultrabasic rocks, usually classified as peridotites and pyroxenites, and their metamorphic equivalents (serpentinites) are Mg-rich subsiliceous rocks that are commonly associated with ophiolite complexes along convergent boundaries of tectonic plates (Brooks, 1987; Oze et al., 2004a). They occupy less than 1% of the Earth's total exposed surface, mainly present in areas within the Circum-Pacific margin and the Mediterranean, and are noted for their elevated levels of Ni, Cr and Co compared with more common aluminosilicate rocks. Most ultrabasic rocks have been partially hydrated or completely serpentinized (Moody, 1976) as a result of their low temperature (300–600 °C) alteration by hydrothermal fluids during detachment from the descending block of oceanic crust and incorporation into subduction mélanges. The mineralogical composition of ultrabasic rocks is dominated by the presence of primary minerals, such as the Fe- and Mg-rich silicate minerals olivine and pyroxene, and oxides (chromite and magnetite). During serpentinization a large variety of metamorphic minerals is formed, represented by the serpentine group minerals (lizardite, chrysotile and antigorite), chlorite, talc, actinolite and tremolite. The majority

of the above minerals may incorporate varying concentrations of Ni and/or Cr into their crystal structures (Oze et al., 2004a).

The chemical weathering of ultramafic rocks (igneous ultrabasic rocks and serpentinites) produces soils that display high levels of Ni and Cr compared to soils derived from non-ultramafic bedrock. Due to the wide distribution and occurrence of ultramafic rocks, concentrations of Ni and Cr in soils are highly variable and are strongly influenced by the geochemistry and mineralogy of the parent material and climatic conditions, as well as other factors including topography, biota and time (Hseu et al., 2007; Kierczak et al., 2007; Lee et al., 2001; Oze et al., 2004b). The slight weathering of ultramafic rocks under a temperate or Mediterranean climate results to the moderate lixiviation of Mg and Si forming secondary Mg-rich or Fe-rich clay minerals, such as Ni- and Cr-bearing smectites, vermiculites and/or chromite–silicate mixtures (Bonifacio et al., 1997; Caillaud et al., 2009; Kierczak et al., 2007; Oze et al., 2004b). Furthermore, amorphous Fe oxides and goethite formed by weathering of clay minerals often accumulate in the soil providing a host for Ni and Cr sequestration (Chardot et al., 2007; Oze et al., 2004b). Despite the occurrence of these secondary minerals, serpentine and spinels inherited from the ultramafic bedrock still remain predominant as Ni and Cr hosts respectively. In such soils that have an ultramafic parent, the bioavailability, mobility and potential toxicity of these two elements are largely depending on the mineral speciation corresponding to their

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chemical binding forms (Cheng et al., 2011; Kierczak et al., 2008; Quantin et al., 2008).

Regional soil geochemical baseline studies reflecting the geogenic concentrations of chemical elements (natural background) and the anthropogenic contribution in soils (Albanese et al., 2007; Galán et al., 2008) are of fundamental significance to estimate the extent of soil contamination, delineate potentially contaminated spots at unsampled areas and to support better decision-making for environmental and human health protection. During the last years, exploratory data analysis (EDA) techniques combining histograms, boxplots and density frequency plots have been widely applied by geochemists enabling a better evaluation of the distributions and features of the data (Bech et al., 2008; Zhang et al., 2008; Zhou and Xia, 2010). In addition, the application of geostatistical methods like the ordinary kriging interpolation and the subsequent production of geochemical baseline maps yield invaluable information on the source, distribution and dynamics of elements in the study area (Guillén et al., 2011).

Recently, Antibachi et al. (2012) reported Ni and Cr concentrations (extracted by aqua regia) up to 2639 mg/kg and 856 mg/kg respectively in agricultural soils of Mouriki–Thiva area, situated in central Greece, attributed to the occurrence and weathering of ultramafic rocks. Such high concentrations may potentially impact the food chain since the agricultural products of this region are a major vegetable supply for Greek population. The present study combines the results obtained by Antibachi et al. (2012) and geochemical results obtained by a new soil sampling campaign in order to produce the geochemical baseline maps of Ni and Cr in these soils naturally enriched with heavy metals. In addition, this paper will collocate Ni and Cr chemical evolution and mineral speciation from the bedrock and the overlying soil along two weathering profiles located in an area where the ultramafic rocks are exposed. Such an integrated approach will shed light on the binding mechanisms of these elements within the soil components and will better define and evaluate the geochemical background. This research is expected to provide the essential geochemical and mineralogical data to forecast the fate of these potentially toxic metals in the soil–plant system of Thiva Valley and their potential leaching to groundwater.

Specific objectives of this study are to: a) identify the Ni- and Cr-bearing minerals in soil horizons and the ultramafic parent that is representative for the study area using a combination of mineralogical and geochemical methods, b) investigate the influence of ultramafic bearing sources on Ni and Cr concentrations in soils from the flat area north of Thiva town as ultramafic weathered rock fragments are transported to the valley, c) get insight into the geochemical data structure of Ni and Cr in Thiva agricultural soils through the application of exploratory data analysis, and d) to obtain spatial analysis soil baseline maps of Ni and Cr and discuss mobility and bioavailability implications.

2. Materials and methods

2.1. Site description and sampling procedure

The study area is located in central Greece northern Thiva town (Fig. 1), with an altitude ranging between 100 m and 250 m, and was selected for its environmental and public health concerns; intense agricultural activities are concentrated in Thiva Valley and primarily include the production of carrots, potatoes and onions. Despite the elevated heavy metal content in soils of Thiva Valley as presented by Antibachi et al. (2012), the characteristic strong chemical fertility limitations and the unique flora of soils developed from ultramafic rocks (Alexander, 1988) are missing due to mixing with non-ultramafic derived constituents. Based on XRD spectrum and scanning electron microscopy observations of selected soil samples from the valley (Antibachi et al., 2012; Galanos, 2011), minerals representative of the ultramafic rocks predominate with respect to those

of the surrounding schists and carbonate rocks. Climate of the area is of Mediterranean type with mild winters and warm, dry summers.

From a geological point of view, the stratigraphic column consists of Triassic to middle Jurassic carbonate sequences (limestones and dolomites) that overlain by the late Jurassic schist-hornstein formation (Papanikolaou, 1990, 2009; Tataris et al., 1966). The latter is a distinct lithological unit including ophiolites, shales, sandstones, clays and limestone layer intercalations. The ultrabasic rocks, which are partially or completely serpentinized, mainly crop out in the vicinity of Ypato and Mouriki villages (Fig. 1) and are part of ophiolite suites dominating in central and northern Greece. Limestones of Cenomanian–Turonian age outcrop north of Yliki Lake and have been unconformably emplaced over the underlying formations (Papanikolaou, 2009). The Quaternary deposits are characterized by the presence of alluvial deposits that floor most part of Thiva Valley whereas Pliocene–Pleistocene sediments consisting of marls, clays, sandstones and conglomerates cover the eastern part of the valley.

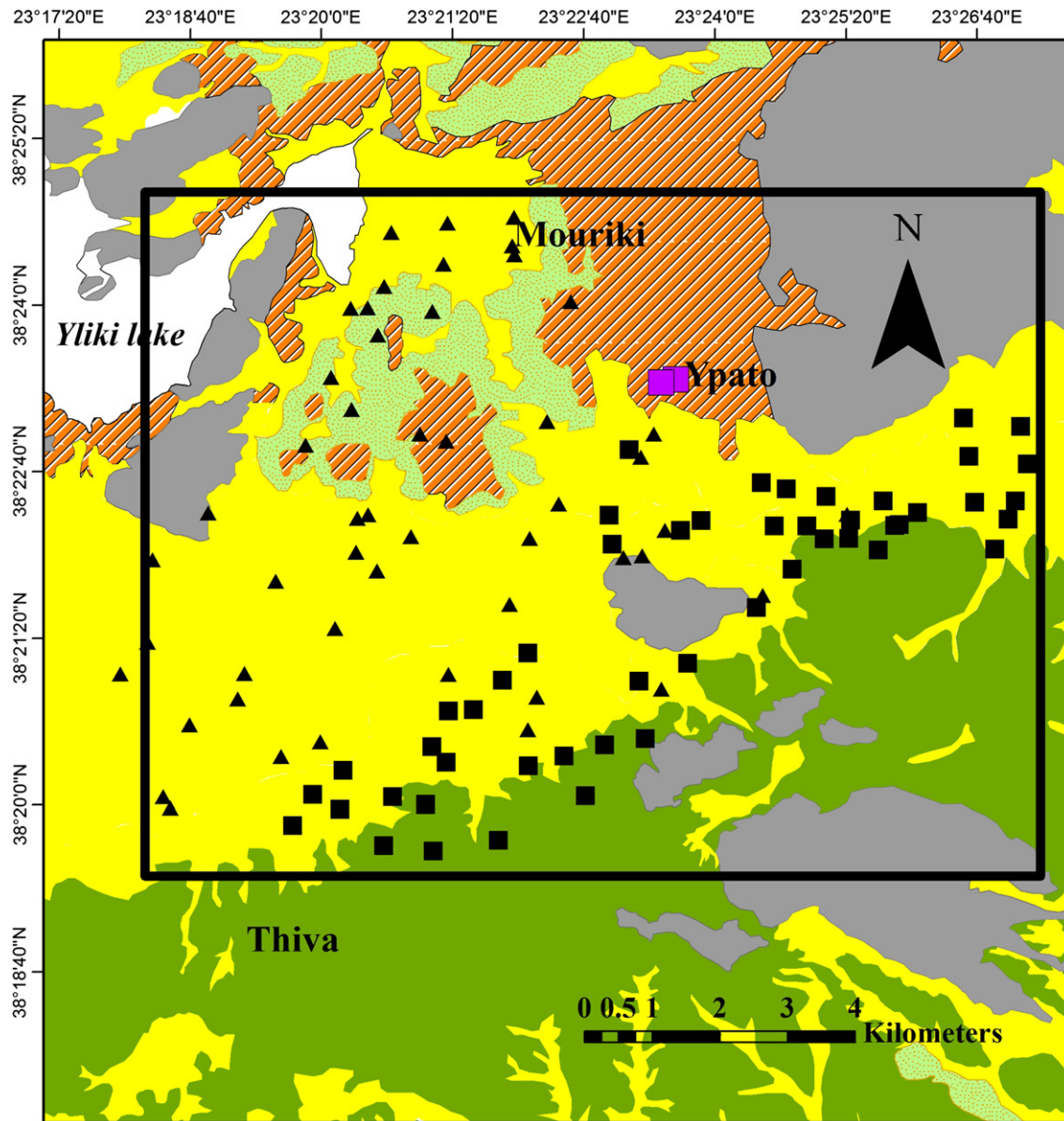
The two investigated weathering profiles are located in a hilly landscape near the Ypato village (Fig. 1) with a distance approximately of 200 m between each other. Small bodies of the ultramafic bedrock are exposed in a stream west of Ypato covering an area of about 0.5 km² and were considered to represent a reasonable approximation of the geochemistry and mineralogy of the ultramafic parent. The soils formed immediately above the parent rocks are not well developed and are only composed of one thin soil horizon. One sample from each soil horizon coded as TB and TIB (approximately at 40 cm depth) and the corresponding underlying parent rocks at 2 m depth (samples TA and TIA respectively) were collected from the two profiles and subsequently analyzed for their chemical and mineralogical composition. The sample sizes were about 5 and 2 kg for rocks and soils respectively.

Soil sampling in Thiva Valley was conducted in 2009 (Antibachi et al., 2012) and in 2010 (50 samples) during a follow-up fieldwork period (Fig. 1). For logistical reasons, the sampling was performed near (~100 m) rural roads and the soils sampled were considered to be representative of the surrounding area. The land use of the area is exclusively agriculture and the valley represents one of the most productive regions of central Greece. A total of 100 topsoil (0–15 cm) samples of about 2 kg were recovered following a random strategy mainly aiming to cover the agricultural area of alluvial soils located north of Thiva town. In order to reduce variability, a composite sample was obtained at each site by collecting material 1 m apart from the vertices of a triangle. At each site, the top 5 cm of plant material and soil were removed and the sample was collected over a depth interval of approximately 5–15 cm. The soil samples were stored in polyethylene bags for transportation and storage and were air-dried at a constant temperature of 40 °C for three days, then sieved through a 2-mm screen and pulverized to a grain size of <0.073 mm in order to focus on size fractions that are potentially most environmentally reactive. The bulk rock samples were crushed, pulverized to recover the same grain size with the soil samples and subsequently homogenized prior to analyses.

2.2. Analytical procedure

2.2.1. Rocks and overlying soils (Ypato site)

Bulk chemical analyses of rocks and overlying soils were performed at the certified Acme Analytical Laboratories Ltd of Canada using X-ray Fluorescence (XRF) for all the chemical elements of concern with the aim to investigate chemical and mineralogical modifications along the investigated weathering profiles. Rock-forming (Si, Mg, Fe, Al, Ca, Na, K, and Mn) and trace elements (Ni and Cr) are expressed in wt.% oxides and mg/kg respectively. Total digestion of materials was done by melting the samples with lithium metaborate (LiBO₂). The accuracy of chemical analyses was evaluated using two certified reference materials provided by the Acme Analytical Laboratories yielding low values of analytical bias between the measured and the expected values for all the rock-forming chemical elements (Si, Al, Mg, Fe, Al, Ca, Na, K and Mn).



Legend

- Location of sections
- Soil samples collected in 2009
- Soil samples collected in 2010
- Alluvial deposits
- Carbonate rocks
- Eluvial mantle
- Lake
- Pliocene-Pleistocene sediments
- Schist-hornstein formation

Fig. 1. Geological map of the study area with the main lithological units (after Tataris et al., 1966) showing soil sampling sites ($n = 100$) and location of the investigated sections. Ultramafic rocks are embedded within the schist–hornstein formation. The frame indicates the area for which the geochemical mapping was accomplished (Figs. 7 and 8).

Mineral assemblages occurring in the rocks as well in the soil horizons were determined by X-ray diffraction and scanning electron microscopy observations. X-ray powder analyses of bulk rock and

soil samples were completed at the Department of Geology and Geoenvironment (University of Athens) using a Siemens D5005 diffractometer with Cu–K α radiation over the range of 3°–65° 2 θ with

a scanning speed $1.0^\circ 2\theta/\text{min}$. Clay mineral content of soil samples was isolated and investigated in oriented samples after solvation with glycol at 65°C for 72 h. Conditions of these analyses were from 3° to $20^\circ 2\theta$ at a rate of $0.125^\circ 2\theta/\text{min}$.

Carbon-coated thin sections of pulverized rock and resin-impregnated soil (0–2 mm) samples were studied by scanning electron microscope (SEM, Jeol JSM-5660 instrument) equipped with an energy dispersive X-ray spectrometer for analysis (EDS, Oxford Link ISIS 300) mainly at the University of Athens (Department of Geology and Geoenvironment) and additionally at the Institute of Geology and Mineral Exploration in Athens. Operating conditions of the instrument were as follows: accelerating voltage 20 kV, beam current 0.5 nA, working distance 20 mm and counting time 80 s. The Ni and Cr-bearing minerals were identified by proportions of constituent element oxides obtained by the semi-quantitative X-ray point analyses taking into account the results from the X-ray diffraction and the mineral phases that commonly occur in similar types of rocks and soils. The average (calculated as arithmetic means) concentrations of Ni and Cr expressed as wt.% oxides are mainly discussed based on a considerable number of semi-quantitative analyses.

2.2.2. Topsoils of Thiva Valley

Concentrations of Ni and Cr in pulverized soil samples of Thiva Valley from both sampling periods were determined at the Laboratory of Economic Geology and Geochemistry (Department of Geology and Geoenvironment, University of Athens) using an aqua regia ($\text{HNO}_3\text{--HCl}$) digestion followed by flame atomic absorption spectroscopy (FAAS), Perkin Elmer 1100B. Selection of the aqua regia extraction was based on its wide application to studies aiming to investigate regional geochemical patterns. Concentrations of Ni and Cr extracted by aqua regia were also determined for the soil horizon samples (T1B and TB) from the two studied weathering profiles in Ypato area in order to obtain information for the mineral phases that are dissolved by this acid digestion.

The quality of data was evaluated by estimations of precision and accuracy and was assessed equal for the two sampling periods enabling the further processing of the combined data set. Duplicate samples were submitted at an approximate rate of 1 duplicate for every 10 samples. In order to evaluate the analytical precision, the relative percent difference (RPD) was calculated for each pair of duplicates revealing RPD values lower than 20%. Reagent blanks were run at the same rate as the duplicate samples as part of the quality assurance process. The accuracy was evaluated by using a standard reference material (NIST 2709 San Joaquin soil) included randomly in each analytical batch of 20 samples. Acceptable RPD values ($<10\%$) between the measured and the certified concentrations were fulfilled by the two investigated heavy metals denoting a high confidence of the analytical data.

2.3. Statistical analysis and geochemical map production

Statistical treatment of soil data from Thiva Valley was carried out using Minitab. Estimates of descriptive parameters, such as mean, median, range, standard deviation, skewness and kurtosis, as well as the Anderson–Darling normality test were established. This test showed that the two metals do not present a normal distribution ($P < 0.005$) exhibiting distinctive different features concerning their distribution patterns as will be discussed in greater detail later. We also applied exploratory data analysis (EDA) techniques for describing element distribution including the presentation of histogram, boxplot and density frequency plot for each metal (Reimann et al., 2005). The Spearman's correlation coefficient has been estimated to quantify the relationship between Ni and Cr contents.

The software ArcMap v.10.0 (ArcGIS) was used to integrate data layers including the georeferenced sampling points and their respective Ni and Cr concentrations, the geological background of the area

and interpolated geochemical maps. The regional geochemical maps showing the overall distribution patterns of Ni and Cr were created using the Geostatistical Analyst tool for ArcMap (ArcGIS) and the ordinary kriging (OK) interpolation method. The concentration intervals for mapping were selected on the basis of boxplots. The kriging method combines the calculation of an experimental variogram from the input data through model fitting and the prediction at unsampled locations (Burgos et al., 2006).

In this study, variograms were calculated using the exponential model setting the majority of the near origin points up to a lag distance of 50 m. Even though normality is not strictly required, serious violation of normality expressed by the presence of outliers can impair the variogram structure and kriging results (McGrath et al., 2004). As a result, observations from the application of exploratory data analysis to the raw Ni and Cr soil data were taken into account before implementation of the geostatistical techniques. Cross validation was based on the estimation of scatter plot between the actual and the kriged predicted Ni and Cr concentrations. This process involves the removal of a value from the dataset and using the remainder of the dataset to estimate that value (Hooker and Nathanail, 2006). Furthermore, a cross validation error map was produced between the measured and the kriged estimated Ni and Cr concentrations according to the ArcGIS kriging output results.

3. Results and discussion

3.1. Parent rock and overlying soils (Ypato site)

3.1.1. Bulk concentrations of major and trace elements

Results of XRF analyses for the whole rocks and the overlying soil horizons in Ypato site ($n = 4$) are listed in Table 1 informing about the chemical composition of the bedrock to which the composition of soil samples will be compared. The bedrock samples exhibit high magnesium (41.4 wt.% MgO) and silicon (~ 43 wt.% SiO_2) contents but iron also occurs in appreciable amounts (~ 8.25 wt.% Fe_2O_3). As expected, concentrations of Al, Ca, Na and K are very low confirming the ultramafic nature of the parent rocks. Weathering of the investigated rocks has produced soil horizons that contain significantly lower Mg contents (average 15.6 wt.% MgO). On the other hand, iron, aluminum, potassium and manganese amounts show a chemical contrast between the bedrock and the soil increasing their contents upwards the soil profile. The soil samples present high levels of Ni and Cr compared to their respective values in Earth's crust originating from the underlying rock (Table 1). Nickel concentrations increase upwards the soil in both studied profiles (up to 3800 mg kg^{-1}) whereas Cr in soils either presents an impoverishment (Profile A, Table 1) or a slight rise (Profile B, Table 1) with respect to parent rocks.

3.1.2. Mineral composition and identification of the various Ni- and Cr-bearing phases

X-ray diffraction spectra of the ultramafic bedrock revealed the occurrence of Mg-rich olivine (forsterite), serpentine (lizardite and/or chrysotile) and orthopyroxene (enstatite) as the major mineral phases. Amphibole (actinolite) and talc occur subordinately whereas traces of smectite were identified in TA sample indicating that the rock samples should be better considered as weathered materials. According to the intensity of the major peak for each identified mineral, a rough approximate quantification of the minerals present in the investigated parent rocks and overlying soils is given in Table 2. However it is significant to mention that this table is only for indicative purposes because the intensity of peaks are not proportional to the quantity of minerals present but rather to other factors like crystallinity of the mineral phases involved.

The XRD spectrum of the soil horizons showed the predominance of serpentine followed by smectite (Table 2); existence of smectite was evidenced by the characteristic expansion of peak from 15 \AA to

Table 1
XRF results (n = 4) for bulk chemical composition of ultramafic parent rocks and overlying soil horizons for the two investigated weathering profiles (Ypato site). The values in parentheses for Ni and Cr in soil samples correspond to concentrations extracted by aqua regia.

	Rock-forming elements (wt.% oxides)								Trace metals (mg kg ⁻¹)	
	SiO ₂	MgO	Fe ₂ O ₃	Al ₂ O ₃	CaO	Na ₂ O	K ₂ O	MnO	Ni	Cr
<i>Profile A</i>										
TB (soil horizon)	43.2	18.28	15.35	3.17	0.57	0.05	0.33	0.25	3800 (3432)	2437 (278)
TA (parent rock)	43.6	41.40	8.18	0.59	0.49	0.02	<0.01	0.12	2540	3176
<i>Profile B</i>										
T1B (soil horizon)	46.3	12.95	14.56	6.11	0.57	0.26	1.03	0.24	3350 (3030)	3442 (317)
T1A (parent rock)	43.0	41.42	8.32	0.98	1.14	0.01	<0.01	0.12	2430	3101
Earth's crust ^a									75	100

^a Earth's crust trace metal amounts are by Levinson (1974).

18 Å after glycolation (Fig. 2). On the contrary, no vermiculite has been detected in any of the soil horizons. In contrast to serpentine which is preserved in the soil, olivine almost disappears denoting that this mineral is probably less resistant to weathering. Illite also occurs as a minor constituent in agreement with the increase in potassium content observed from the parent rocks to the soil samples (Table 1). Weak reflections of magnetite and hematite occur in the T1B soil sample whereas relics of enstatite still remain in TB soil as a minor phase. Allogenic minerals like quartz and Na-rich feldspar (albite) are present reflecting contamination by non-ultramafic components (nearby schists), probably as a result of eolian deposition.

X-ray semi-quantitative analyses of minerals in the ultramafic parent demonstrate that the main Ni-bearing phases are olivine and serpentine; NiO content reaches up to 0.6 wt.% (average 0.5 wt.% or 3930 mg/kg Ni) and up to 0.5 wt.% (average 0.4 wt.% or 3140 mg/kg Ni) respectively (Table 3). On the contrary, Cr-containing minerals within the bedrock (Table 3) include chromite (average 40.5 wt.% of Cr₂O₃), enstatite (average 0.5 wt.% of Cr₂O₃ or 3420 mg/kg Cr), diopside (average 0.7 wt.% of Cr₂O₃) and actinolite that hosts significant amounts of Cr (up to 1.6 wt.% of Cr₂O₃). Predominance of chromite (the most enriched mineral with respect to Cr) and enstatite that contains the least Cr is evident compared to actinolite and diopside. Occasionally, serpentine grains contain little Cr (~0.3 wt.% of Cr₂O₃ or 2050 mg/kg Cr) but their contribution to the Cr enrichment of the investigated ultramafic bedrock should be considered as negligible.

According to EDS measurements both overlying soil horizons display a similar mineralogical composition that is different from that identified for the bedrock including the occurrence of secondary mineral phases, like smectite, goethite and to a lesser extent hematite and Mn-oxides (Table 4 and Fig. 3). The serpentine minerals in soils exhibit a slight increase in NiO content (average 0.5 wt.% or 3930 mg/kg Ni) compared to those determined in the weathered parent rocks. In contrast to other studies (Kierczak et al., 2007), the serpentine minerals from the soil horizons are not depleted in Mg and Si; in addition, they preserve their occasional low Cr contents. In agreement with Quantin et al. (2008) who studied soil profiles developed from serpentinites in Czech Republic, olivine almost disappears in the investigated soil horizons confirming the low resistance of this mineral to weathering and

the impoverishment of Mg with respect to bedrock (Table 1). When preserved, olivine exhibits a decrease in NiO content (average 0.3 wt.% or 2360 mg/kg Ni). Primary enstatite still remains in the soils increasing its Cr content (average 0.8 wt.% of Cr₂O₃ or 5470 mg/kg Cr) whereas chromite grains present a chemically distinct composition compared to bedrock; in particular, they contain significant higher concentrations of Cr (average 54.7 wt.% of Cr₂O₃ compared to 40.5 wt.% of Cr₂O₃ in bedrock) and an accompanying reduction in Al amounts (average 12.6 wt.% of Al₂O₃ compared to 26.0 wt.% of Al₂O₃ in bedrock). Interestingly, some Cr-magnetite was identified in the soils, with an average of 12.2 wt.% of Cr₂O₃. It is chemically distinguished from chromite by its higher concentration of Fe and Si and the lower contents of Cr (Table 4). Occurrence of magnetite in the soil horizons should be attributed to its recalcitrance to chemical weathering compared to the silicates of the bedrock samples (Fandeur et al., 2009).

The scanning electron microscopy studies revealed that smectites contain varying amounts of Ni with a maximum of 1.0 wt.% NiO (average 0.5 wt.% of NiO) representing the most predominant Ni enriched mineral phase in the investigated soil horizons (Table 4). Smectites commonly replace serpentine (Fig. 3a) or olivine when still present representing their usual products at the first stages of chemical weathering. In contrast to Garnier et al. (2009) who reported significant Cr contents in smectites formed by weathering of ultramafic parent under tropical conditions, smectites in the studied soils from Ypato site do not contain Cr, at least at the quantification limit.

As chemical weathering progresses, iron oxides such as goethite and hematite are formed (Fig. 3b), probably as a result of Fe release during alteration of olivine and/or serpentine (Chardot et al., 2007). Goethite systematically contains appreciable amounts of Ni averaging 1.1 wt.% of NiO (Table 4) and in rare cases carries very low concentrations of Cr. Together with smectites, goethite is the mineral presenting a high level of Ni accumulation in the studied soils. Based on chemical modifications and appearance, two types of goethite can be discriminated: the first one is Si-rich (Fig. 3b) whereas the second population is Si-poor (Fig. 3c). The first group seems to be more enriched with respect to Ni because the adsorbed silica can retard the crystal growth of goethite favoring the sequestration of Ni (Becquer et al., 2006). However, it is unclear whether Ni is incorporated in the crystal lattice of goethite or

Table 2
Relative abundance of crystalline minerals present in the investigated parent rocks and the overlying soils according to X-ray diffraction.

	Serpentine	Olivine	Enstatite	Actinolite	Talc	Smectite	Illite	Magnetite	Hematite	Quartz	Albite
<i>Profile A</i>											
TB (soil horizon)	++		+			+++	+			+	
TA (parent rock)	++	+++	+++	+	+	+					
<i>Profile B</i>											
T1B (soil horizon)	++					++	+	+	+	++	+
T1A (parent rock)	++	+++	+++	+							

+++ abundant, ++ moderate, + minor or trace.

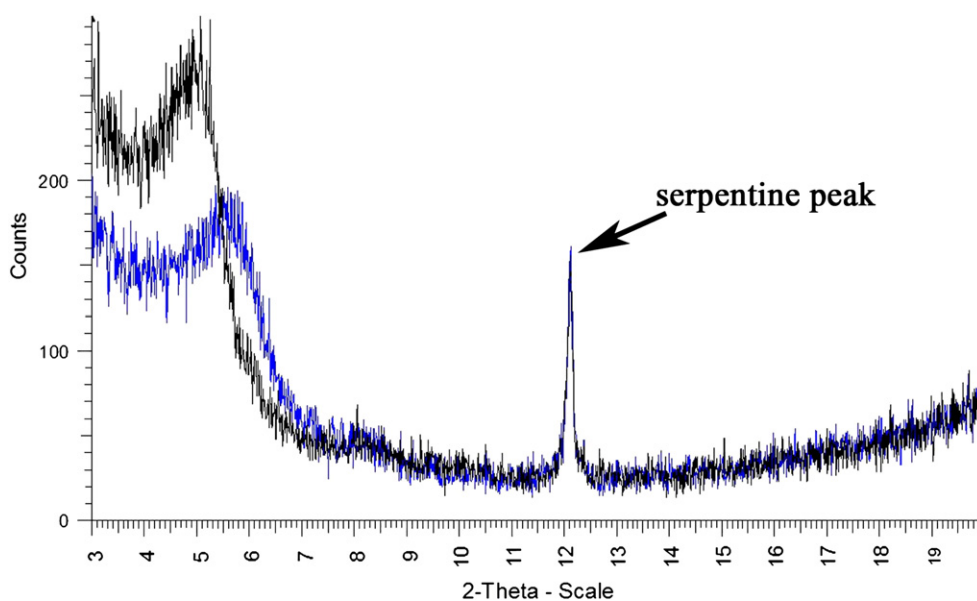


Fig. 2. Oriented XRD powder pattern of untreated (blue color) and ethylene glycol solvated (black color) soil horizon sample from Ypato site showing the characteristic expansion of smectite peak from 15 Å to 18 Å after glycolation.

is sorbed onto its surface, a fact that will have significant implications for the bioavailability of Ni in the studied area. The relatively low concentrations of Ni (0.6–1.9 wt.% of NiO, Table 4) within goethite found in this study may be an indication that Ni is probably most complexed onto goethite surface (Massoura et al., 2006). On the other hand, the identification of few goethite grains with higher amounts of Ni (up to 5.0 wt.% of NiO) in soils from Thiva Valley (Galanos, 2011) signifies that some Ni has entered the lattice of goethite through substitution. When formed, hematite contains minor concentrations of Cr and/or Ni.

The SEM/EDS observations also revealed that Mn (hydr)oxides grains contain significant Ni concentrations (Fig. 3d), a mineral phase that was also found in agricultural soils from Thiva Valley (Antibachi et al., 2012). Despite their substantial lower abundance compared to Fe oxides, Mn oxides encompass a higher adsorption capacity and recent studies have shown that when present in serpentine soils they largely determine the Ni sorption capacity and bioavailability, in the case however of low clay mineral content (Alves et al., 2011).

In conclusion, weathering processes of primary phyllosilicate minerals in the investigated ultramafic parent rocks has resulted to the

formation of new minerals in overlying soil horizons that contain Ni concentrations higher than parent bedrock. A contrasting behavior is observed for Cr; the main Cr-bearing minerals within the soils are inherited minerals that are not susceptible to weathering.

3.2. Topsoils of Thiva Valley

3.2.1. Metal content and exploratory data analysis

A statistical summary of the Ni and Cr concentrations for alluvial soils of Thiva Valley is given in Table 5. The high value of standard deviation for Ni signifies that the soils exhibit a large variability regarding their Ni content (minimum and maximum values are 299 mg/kg and 2640 mg/kg respectively) with a median of 1390 mg/kg. Chromium values are significantly lower (median 299 mg/kg) presenting maxima of 856 mg/kg. The higher value of skewness for Cr indicates that the majority of Cr concentrations are concentrated on the low values (Zhou and Xia, 2010).

Nickel is present in studied soils at levels which can be considered that are typical for soils that have an ultramafic parent (Table 5). A

Table 3

Average (arithmetic mean) chemical composition for the identified minerals containing Ni and Cr in the investigated parent rocks according to semi-quantitative EDS analyses. The number of analyses mostly corresponds to individual mineral grains.

Wt.%	Olivine	Serpentine	Enstatite	Diopside	Actinolite	Chromite
SiO ₂	41.7 [39.2–47.4]	39.7 [36.3–41.9]	55.1 [51.9–57.7]	54.8 [52.2–60.1]	50.9 [50.7–52.3]	0.6 [0.4–1.1]
MgO	48.2 [47.3–49.4]	36.2 [33.1–38.7]	34.0 [31.8–35.8]	17.6 [16.9–19.0]	17.3 [16.1–17.6]	12.2 [11.4–17.2]
FeO	9.1 [8.5–10.1]	5.9 [4.2–8.5]	6.1 [5.8–6.7]	1.8 [1.6–1.9]	3.0 [2.6–3.2]	18.5 [14.0–19.9]
Al ₂ O ₃		1.0 [0.7–1.5]	2.2 [1.1–3.0]	1.8 [0.9–2.4]	8.3 [8.0–8.8]	26.0 [17.9–41.1]
CaO			0.4 [0.2–0.6]	24.0 [23.5–24.6]	11.9 [11.4–12.0]	
Na ₂ O					1.3 [1.3–1.4]	
NiO	0.5 [0.4–0.6]	0.4 [0.4–0.5]				
Cr ₂ O ₃		0.3 [0.3–0.3]	0.5 [0.3–0.9]	0.7 [0.5–1.0]	1.6 [1.6–1.6]	40.5 [23.1–50.7]
n	14	22	13	8	4	19

n = number of analyses, [a–b] = concentration range.

Table 4
Average (arithmetic mean) chemical composition for the identified minerals containing Ni and Cr in the investigated soil horizons according to semi-quantitative EDS analyses. The number of analyses mostly corresponds to individual mineral grains.

Wt.%	Olivine	Serpentine	Enstatite	Chromite	Magnetite	Smectite	Goethite	Hematite
SiO ₂	38.9 [38.1–39.9]	44.5 [38.3–46.0]	55.2 [53.3–57.6]	0.6 [0.3–0.8]	7.2 [2.3–11.6]	49.5 [40.6–61.7]	5.1 [0.6–13.4]	1.1 [0.7–1.7]
MgO	48.1 [48.0–48.9]	37.2 [31.8–40.8]	32.4 [29.2–34.5]	10.1 [7.6–13.1]	6.5 [1.5–10.8]	8.4 [4.2–19.3]	3.7 [0.5–8.4]	1.0 [0.6–1.4]
FeO	8.3 [7.0–8.6]	6.1 [4.7–7.0]	5.9 [5.5–6.6]	21.6 [18.2–27.4]	66.9 [48.3–82.1]	18.8 [14.5–26.6]		
Fe ₂ O ₃							79.6 [60.9–90.1]	97.5 [95.6–104.0]
Al ₂ O ₃		0.5 [0.5–0.7]	3.1 [2.2–3.8]	12.6 [4.5–26.8]		7.3 [5.6–10.2]	0.8 [0.3–1.7]	
CaO			0.7 [0.4–1.3]		0.3 [0.2–0.3]	0.6 [0.4–0.9]	0.4 [0.2–0.6]	
K ₂ O						1.3 [0.4–1.9]		
NiO	0.3 [0.3–0.4]	0.5 [0.4–0.9]				0.5 [0.3–1.0]	1.1 [0.6–1.9]	
Cr ₂ O ₃		0.3 [0.3–0.3]	0.8 [0.7–1.3]	54.7 [36.8–67.6]	12.2 [6.7–17.7]			0.3 [0.3–0.5]
MnO							1.5 [0.7–2.1]	0.5
n	4	13	8	15	4	24	14	5

n = number of analyses, [a–b] = concentration range.

higher mean content for Ni is found in serpentine soils from the Coast Range Ophiolite in California (Morrison et al., 2009) and central Euboea in Greece (Megremi, 2010) ascribed either to the more widespread participation of Ni-bearing minerals or to the occurrence of Fe–Ni laterite deposits respectively. Chromium concentrations in topsoils of Thiva Valley fall within the lowest values reported in the literature for soils developed from ultramafic rocks (Table 5) as a result of the applied decomposition method that is sufficient to release only a small amount of the total Cr present in the soil (see the aqua regia extractable concentrations of Cr in soil horizons from the investigated

weathering profiles in Ypato area, Table 1). The main Cr-bearing minerals identified in this study such as the spinels and enstatite are unaffected by the aqua regia digestion; the reported Cr values are likely the result of dissolution of Cr trace amounts found in serpentine. On the other hand, all the major mineral hosts of Ni (serpentine, smectites and goethite) are preferentially decomposed by the aqua regia explaining the high Ni amounts determined in topsoil samples of the valley and the slightly lower Ni values obtained by the acid extraction in the soil horizons from Ypato site compared to the XRF results.

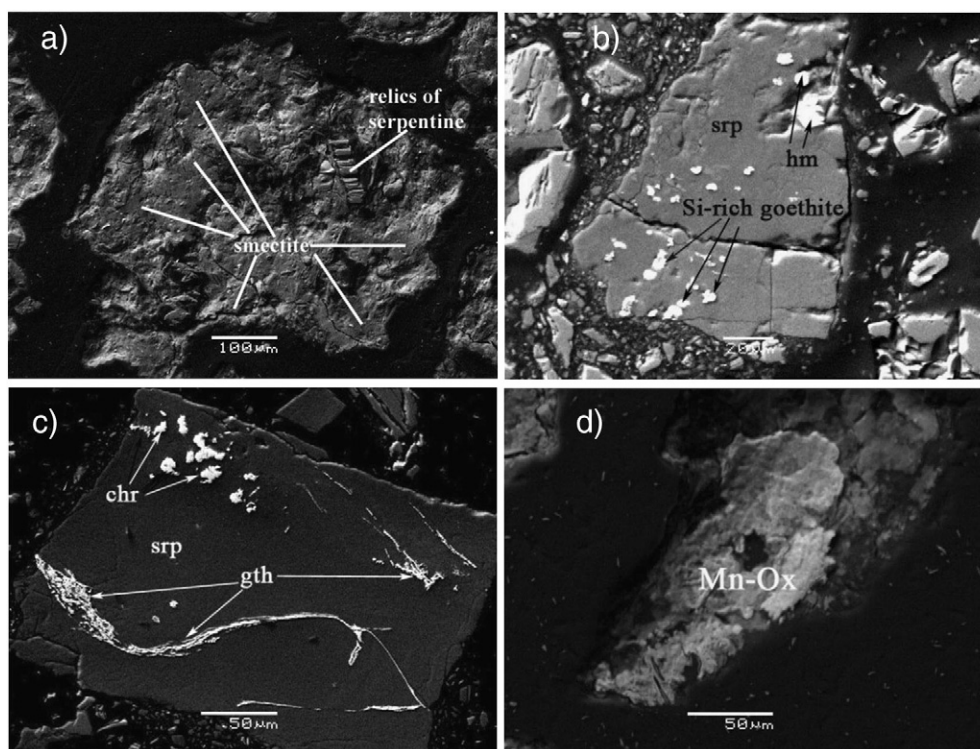


Fig. 3. Backscattered electron images of Ni- and Cr-bearing minerals in the investigated soil horizons: a) smectite occurrence with up to 0.8 wt.% of NiO replacing serpentine, b) Si-rich goethite with 1.0 wt.% of NiO and hematite with traces of Cr₂O₃, c) Si-poor goethite containing up to 0.6 wt.% of NiO, d) Mn oxide containing up to 3.8 wt.% of NiO. Abbreviations: srp → serpentine, chr → chromite, gth: goethite, hm: hematite, Mn-Ox: Mn-oxide.

Table 5

Statistical summary of Ni and Cr concentrations (mg/kg) extracted by aqua regia in agricultural topsoils of Thiva Valley (n = 100). Data are from the present study and Antibachi et al. (2012). Geochemical data (mean values) for ultramafic rocks and soils with an ultramafic parent and the Dutch intervention limits are also presented for comparison purposes.

	Ni	Cr
Mean	1390	299
Median	1315	273
Standard deviation	624	115
Min	299	134
Max	2640	856
Skewness	0.26	2.41
Kurtosis	-1.11	8.79
First quartile	849	235
Third quartile	1976	351
Mean in ultramafic rocks ^a	2000	1600
Central Euboea, Greece ^b	2800	1300
Coast Range Ophiolite, California ^c	2505	1365
NW Italy (Alpine soils) ^d	907	822
Susaki, Greece ^e	994	920
Intervention limits (Dutch law) ^f	210	380

^a Turekian and Wedepohl (1961).

^b Megremi (2010).

^c Morrison et al. (2009).

^d Bonifacio et al. (2010).

^e Kelepertzis et al. (2001).

^f VROM (2000).

Considering the intervention limits of Dutch legislation (Table 5) that are frequently applied to soil and stream sediment geochemical environmental studies, it becomes evident that all the collected soils have Ni values above the corresponding limit whereas Cr concentrations for approximately 20% of the samples also exceed the limit of 380 mg/kg. However, the main disadvantage of the Netherlands quality criteria is they do not take into account either the land use of the area or, more significantly, the binding mechanisms of the metals within the soil constituents that largely determine the potential environmental effects.

The Anderson–Darling normality test evidenced that both the investigated metals do not present a normal distribution ($P < 0.005$). The application of exploratory data analysis (EDA) provides an invaluable tool for describing the elements distribution. Histograms provide a graphical summary of the data distribution but boxplots are more useful because they give a better insight into the data structure and the presence of possible outliers (Chiprés et al., 2009). In addition, density frequency plots indicate the occurrence of various subpopulations with breaks or inflections in the data distribution, which in the absence of hardly any anthropogenic activities, are the consequence of different geological substrate in the area (Mrvić et al., 2011). The EDA diagrams generated in this study are presented in Fig. 4. The constructed histograms show that geochemical data for both elements have an asymmetrical distribution; however, Ni presents a bimodal distribution whereas Cr has a right skewed distribution tendency. This is also confirmed by the lower value of kurtosis for Ni compared to Cr (Table 5).

Inspection of boxplots and density frequency plots demonstrates the presence of two outliers in the Cr data set (defined as values that exceed the expected distribution range) which are not the same as in the case of Ni (see the density frequency plot for Ni). Omitting the two outliers from the Cr data set and generating EDA diagrams again (Fig. 5) has as a result the occurrence of a substantial number of outliers in the remaining data. Outliers are commonly ascribed to anthropogenic influences eliminating natural geogenic anomalies. However, in this study the high Cr concentrations expressed as outliers when performing the EDA diagrams should be attributed to a local greater contribution of Cr-bearing minerals within the soil that can be partially dissolved by the aqua regia extraction method. Such mineral phases may include some preserved olivine and/or serpentine containing

increased amounts of Cr, or smaller strongly weathered enstatite or spinel grains of high surface area (Morrison et al., 2009).

Based on the inflection points that are revealed by the density frequency plots, two major sub-sets can be identified for the Ni data: 299–1910 mg/kg and > 1970 mg/kg. For Cr two general subpopulations are distinguished without taking account the two outliers of the whole geochemical data, however the break is not as distinct as in case of Ni: 134–300 mg/kg and 330–490 mg/kg. These two groups of samples for each metal are closely linked with the abundance of the various mineral phases that host Ni and Cr within the soils and are capable to release their Ni and Cr content when attacked by the HNO₃–HCl acid mixture. Moreover, the heterogeneity in chemical composition of the bedrock strongly supports the occurrence of two subpopulations for Ni and Cr enrichment in the studied soils. Except for the ultramafic rock outcrops, the surrounding geological formations involve the occurrence of chemically and mineralogically distinctive parent materials i.e. schists and carbonate rocks. As a result, the relatively low Ni and Cr values of the first subpopulation are related to the fact that the Ni- and Cr-bearing minerals are likely to be scattered reflecting greater dilution by appreciable volumes of the non-ultramafic derived constituents. The mineralogical forms of these components are represented by the presence of quartz, feldspars and calcite within the topsoils of Thiva Valley (Antibachi et al., 2012; Galanos, 2011).

3.2.2. Geochemical mapping

Observations of EDA diagrams for Ni and Cr raw data set revealed the necessity for log-transformation of Cr values to ensure that the input for kriging data were almost normally distributed. Interpolation of non-normally distributed data may amplify the variogram fluctuation and increase the estimation error (Yuan et al., 2012). The log-transformed data were used for interpolation and the results were then back transformed with the reverse process in order to produce the final spatial Cr distribution map.

The cross validation procedure for evaluating the effectiveness of the variogram model as a measured-kriged estimated scatter plot and as a spatial error map are presented in Figs. 6 and 7 respectively. In Fig. 6, points above the line reflect an overestimation whereas points below the line indicate an underestimation. Few high and low Ni and Cr concentrations were significantly underestimated or correspondingly overestimated by the remaining data. However, a good linear relationship between the actual and the estimated concentrations is obtained for both metals indicating that the observed values were generally well estimated. The spatial error maps (Fig. 7) do not show a systematic trend either of underestimation or of overestimation with respect to Ni and Cr values.

The soil surface contour maps for the investigated metals are illustrated in Fig. 8. Interestingly, the spatial distribution patterns for the two elements are not similar despite their common origin which is the occurrence of ultramafic rocks. In particular, the highest Ni concentrations (> ~2000 mg/kg) are found in the northern part of the area where the ultramafic rocks outcrop; conversely to Ni, Cr mainly demonstrates its elevated content (> ~350 mg/kg) in the southern part of the area. However, another hotspot area with large Ni concentrations is concentrated in the southern part. The geochemical baseline maps signify that the elevated concentrations of Ni and Cr in the alluvium agricultural topsoils of Thiva Valley are the result of mechanical transport of these elements from their serpentinite sources exposed in Ypato and Mouriki sites. According to Bonifacio et al. (2010), even small amounts of serpentines can induce metal contents above 200 mg/kg. Furthermore, the spatial distribution of Ni and Cr alarms about the potential high metal levels in soils of Thiva town which is located a few kilometers south.

The general contrasting spatial variation of Ni and Cr concentrations is strengthened by the weak correlation coefficient between the two metals (Fig. 9) that can be attributed to the different minerals

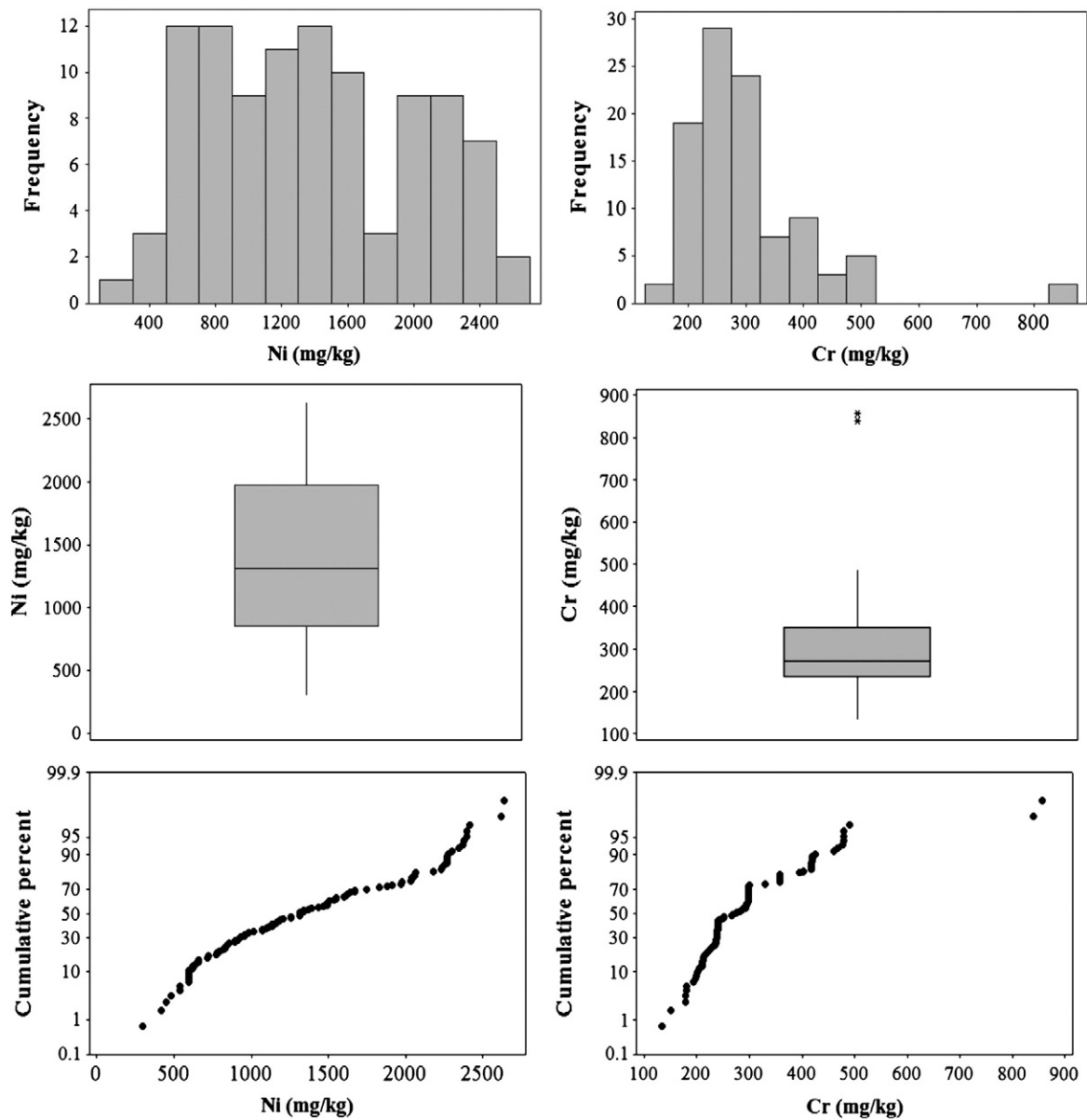


Fig. 4. Graphical inspection of Ni and Cr concentrations through EDA diagrams: histograms, boxplots and density frequency plots. Data are from the present study and [Antibachi et al. \(2012\)](#). For the boxplots, the length of the box indicates the interquartile range, the horizontal line inside the box indicates the median, the whiskers extend to the maximum and minimum data point within 1.5 box heights from the top or the bottom of the box and outliers are concentrations beyond the upper whisker.

that host Ni and Cr within the soils. Removing the outliers from the Cr data set and calculating the correlation coefficient again results to even lower value of the coefficient ($r = 0.19$). The weak positive correlation between these two elements has previously been reported by [Kierczak et al. \(2007\)](#) who compared Ni and Cr content in soils developed on serpentinites from different sites in Europe. However it should be mentioned that quite a lot of other authors have established strong positive correlations between Ni and Cr and use it as a proof for their geogenic source (e.g. [Galán et al., 2008](#); [Megremi, 2010](#); [Vardaki and Kelepertzis, 1999](#)). The relative effects of aqua regia extraction on different minerals play a key role for Ni and Cr associations. As it has been mentioned, the main Ni-bearing minerals such as the trioctahedral serpentines, smectites and Fe–Mn oxide compounds are more susceptible to aqua regia digestion ([Klassen, 2009](#)) compared to Cr that is participated in the crystal lattice of recalcitrant mineral phases. The applied extraction method dissociates the two elements based on their mineralogical residence to acid-soluble and acid-insoluble forms.

3.2.3. Implications for Ni and Cr bioavailability and potential leaching to groundwater

The differences in mineralogy and chemical reactivity of the identified Ni- and Cr-containing minerals strongly control their potential bioavailability and mobility when these metals have a geogenic origin. More specifically, Ni availability is generally higher when Ni is associated with phyllosilicate minerals compared to well-crystallized Fe oxides formed in intensively weathered soil horizons ([Echevarria et al., 2006](#); [Massoura et al., 2006](#)). The ultramafic silicates, which are relatively unstable under near-surface conditions, release their Ni content that can be adsorbed more easily on the available exchangeable sites of the soils (clays and Fe–Mn oxides) compared to Cr ([Cheng et al., 2011](#)). In the investigated soils except for the contribution of serpentine minerals to the potential high Ni availability, the occurrence of abundant secondary Ni-bearing smectites represents another significant source of potentially labile Ni. Furthermore, liberation of Ni from goethite is not expected to occur if Ni has been

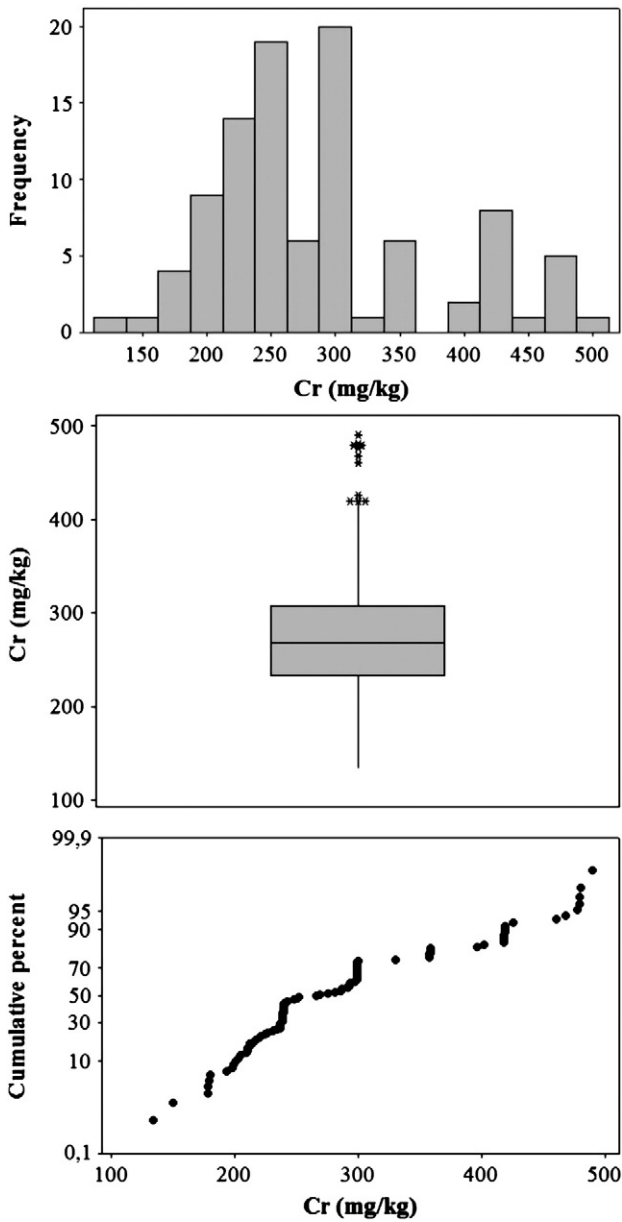


Fig. 5. Generated EDA diagrams for the Cr data set after omitting the two outliers.

sequestered in the mineral matrix (Echevarria et al., 2006); however, whether Ni has entered the mineral structure of goethite or is sorbed onto its surface remains questionable. Although scarcely detected by

SEM observations, Mn oxides with high Ni contents are expected to influence Ni dynamics in the studied soils representing a likely source of chemically labile Ni (Alves et al., 2011; Quantin et al., 2008). The discussed potentially high bioavailability of Ni is in full agreement with the published Ni enrichment of agricultural products (potatoes, carrots and onions) cultivated in Thiva compared to uncontaminated control areas (Kirkillis et al., 2012). Going a step further, the alkaline pH values of both soil (Antibachi et al., 2012; Galanos, 2011) and groundwaters (Tziritis et al., 2012) from Thiva Valley coupled with the determined mineralogical residence of Ni involving adsorption onto clays and/or Fe and Mn oxides explain the almost undetectable levels of Ni in these groundwaters. Mobilization of Ni may occur in isolated areas where the pH conditions will locally decrease.

On the other hand Cr release into the environment is not expected to occur when this metal is found in geochemically inert mineral phases like chromite and magnetite (Kierczak et al., 2008; Oze et al., 2004b). In the soil horizons produced by weathering of ultramafic bedrock in the study area, the major Cr-bearing minerals are inherited chromite and magnetite that are very slowly hydrolyzed and thus Cr is not easily available and is considered to be relatively immobile. Although chromite, the primary mineralogical source for Cr was considered resistant to weathering, recent studies have shown that this mineral is not a completely unweatherable primary mineral and may undergo incongruent dissolution and chemical modifications (Oze et al., 2004b; Garnier et al., 2008; Fandeur et al., 2009). This process may result to the oxidation of Cr(III) within chromite to the more soluble and toxic hexavalent form in the presence of Mn minerals (Oze et al., 2007). As a result, natural oxidation mechanisms may account for the relatively high levels of Cr(VI) that have been determined in the groundwater systems within proximity of ultramafic rocks (e.g. Fantoni et al., 2002; Margiotta et al., 2012; Robles-Camacho and Armienta, 2000) and/or the Cr(VI) values that have determined in ultramafic soils (Becquer et al., 2003; Garnier et al., 2006). Moreover, a recent study (Bertolo et al., 2011) presented high geogenic concentrations of Cr(VI) in groundwaters from an area located in Brazil ascribed to the weathering of diopside grains containing up to 1.2% as Cr_2O_3 that show dissolution features. These authors stated that part of amorphous Mn oxides could be available for oxidizing Cr(III) to Cr(VI). In the case however of Thiva Valley and considering the relatively low Mn content (Table 1), it is more likely that natural processes do not significantly contribute to the abnormally high (up to 212 $\mu\text{g/l}$) Cr(VI) values that have been measured in irrigated groundwaters from Thiva Valley (Tziritis et al., 2012). However, Moraetis et al. (2012) argued that geogenic sources, i.e. alluvial serpentine soils containing erosion products (chromites) of ultramafic rocks, in a geologically similar area located further south of Thiva Valley are capable to produce high concentrations of dissolved Cr(VI). It should also be mentioned that generation rates and leaching of Cr(VI) to groundwater may be enhanced by agricultural activities (Mills et al., 2011) and/or the presence of Cr silicates within the soils (Oze et al., 2007).

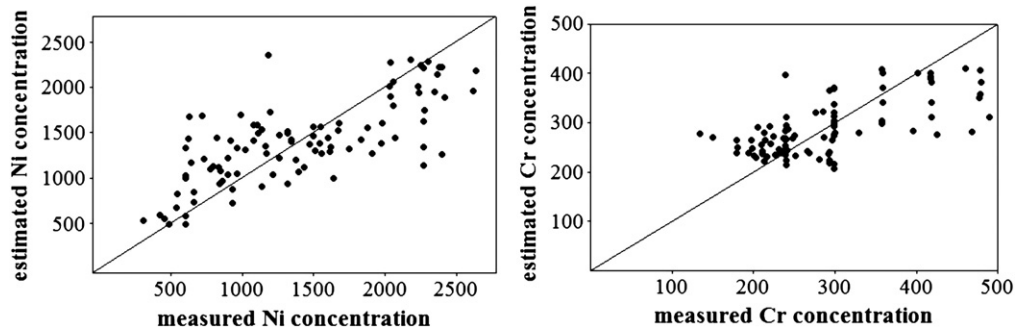


Fig. 6. Cross validation scatter plot between the actual and the kriged estimated Ni and Cr concentrations (in mg/kg) for agricultural soils of Thiva Valley. Measured concentrations are from the present study and Antibachi et al. (2012).

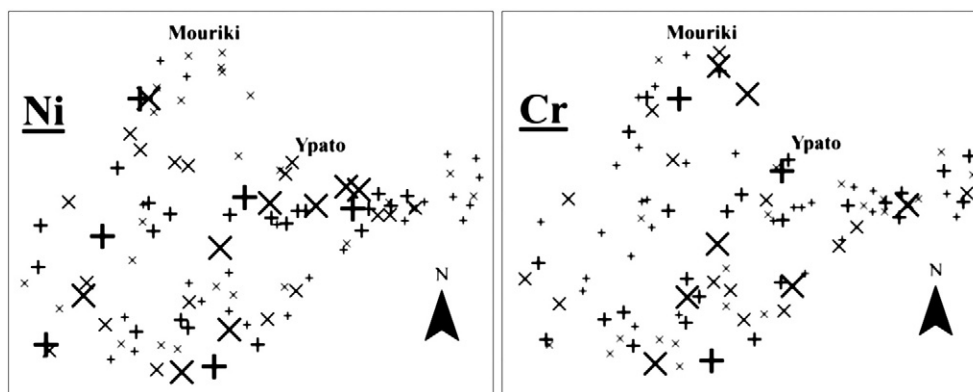


Fig. 7. Cross validation error map between the measured and the kriged estimated Ni and Cr concentrations for agricultural soils of Thiva Valley. The symbol “+” indicates overestimation, whereas the symbol “x” underestimation; the symbol size reflects the magnitude of error. Data are from the present study and Antibachi et al. (2012).

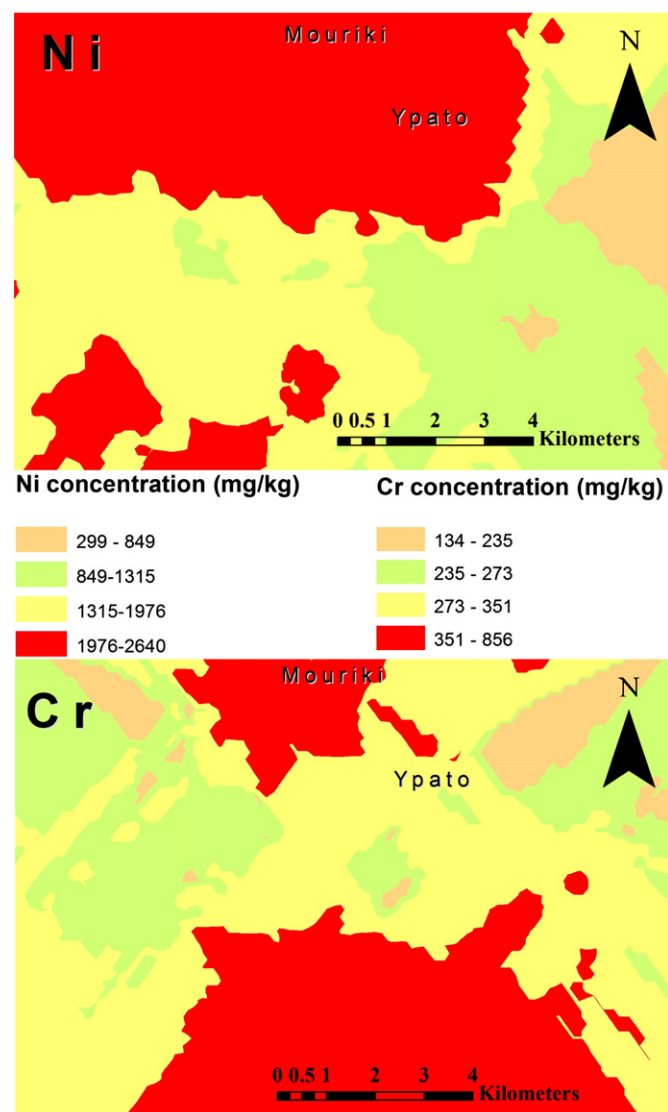


Fig. 8. Geochemical maps of regional baseline concentrations of Ni and Cr in agricultural soils from Thiva Valley produced by the ordinary kriging interpolation method. Chemical analyses come from the present study and Antibachi et al. (2012). Concentration intervals were selected on the basis of boxplots (25th, 50th and 75th percentile).

4. Conclusions

To elucidate the source of the elevated Ni and Cr content determined in agricultural topsoils of Thiva Valley (central Greece) in a previous environmental geochemical study, the chemical and mineralogical evolution of these metals from representative ultramafic bedrock and overlying soil horizon along two weathering profiles was investigated. The studied ultramafic parent is a typical serpentinite that exhibits large amounts of Ni and Cr. The soils derived from this natural trace metal-bearing rock display a significant Ni enrichment compared to bedrock whereas Cr preserves or either decreases its content. The mineral speciation of Ni within the soil horizons signified the occurrence of different Ni-bearing mineral phases including serpentines originated from the bedrock and secondary smectites and Fe–Mn oxides. The neoformed phases were found to contain Ni concentrations significantly higher than minerals within the original bedrock. By comparison, most Cr in soils from the studied profiles occurs in primary inherited minerals (chromite and to a lesser extent magnetite) whereas the Cr silicates and Cr-containing hematite account only for a low percent of the total soil Cr.

The regional geochemical research of Ni and Cr in alluvial agricultural topsoils of Thiva Valley demonstrates that geochemical anomalies are the result of mechanical transport of weathered rock fragments from the upslope ultramafic parent. The geochemical baseline maps produced by the ordinary kriging interpolation method indicate a general contrasting spatial distribution for the two elements attributed to the local abundance of aqua regia soluble minerals hosting Ni and Cr and dilution from surrounding non-ultramafic derived components. Based on their solid speciation, Ni bioavailability is likely to be high and controlled by the identified soluble phases whereas Cr availability is

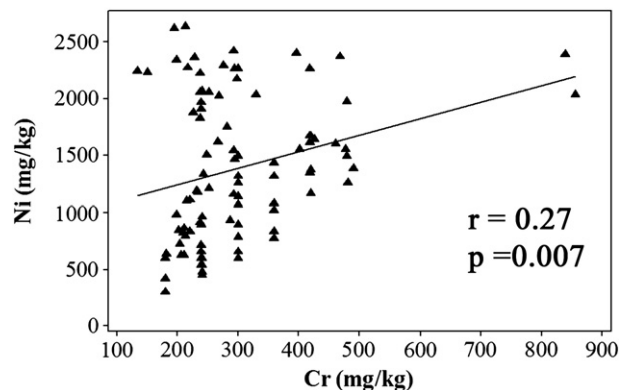


Fig. 9. Correlation diagram of Ni and Cr content in agricultural soils of Thiva Valley. Data are from the present study and Antibachi et al. (2012).

expected to be low as a result of its significant incorporation in the crystal lattice of primary stable minerals. However, their leaching to groundwater will also be governed by the pH and redox conditions of the soil–groundwater system and the potential of oxidizer agents to generate oxidized Cr from Cr(III)–rich minerals.

Results of this study emphasize the importance of accurate identification of specific mineral phases that host Ni and Cr in soil geochemical studies not only for simplifying the interpretation of geochemical background variation, but also for providing information about their potential mobility and bioavailability. Consequently in the case of high geogenic ultramafic-derived Ni and Cr concentrations the mineral speciation dynamics is essential in societal decision-makings whereas the comparison of international threshold limits for soil quality with metal contents should be avoided because the high concentrations do not necessarily imply negative environmental effects. Finally, this study also signifies the strong influence of the applied analytical decomposition method on Ni and Cr concentrations in soil environments that are naturally enriched with these metals.

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