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ΔΙΠΛΩΜΑΤΙΚΗ ΕΡΓΑΣΙΑ

The lithogeochemical character of near-surface bedrock in the Athens Basin

Λιθογεωχημικός χαρακτηρισμός πετρωμάτων με επιφανειακή εμφάνιση στο Λεκανοπέδιο Αθηνών

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The lithogeochemical character of near-surface bedrock in the Athens Basin

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ABSTRACT

This Thesis presents the results of a lithogeochemical survey conducted in the Athens Basin, Greece. Forty-six rock samples have been collected and analysed. The total concentrations of major and trace elements have been used in order to assess their geochemical associations within the examined rock-types. Moreover, these concentrations were used to investigate the effect of bedrock composition on the PHEs enrichment in Athens soil with special emphasis on As which had been found to be particularly enriched in soil during a previous survey (max concentration about 200 mg/kg). The examined elements include Si, Al, Mg, Mn, Ca, Na, Ti, Fe, P, Cr, Ni, K, Rb, Ba, Th, Pb, Nb, P, Sr, As, Sn, Co, Zn, Cu and Sb. The analyses were conducted using Powder-XRF spectroscopy.

The highest concentrations of arsenic were found in rock samples from the central and western parts of the Athens Basin. The areas that recorded the highest average concentrations are Tourkovounia in the north-central part of the basin and the flanks of Hymettus Mt in the western part of the basin. In these areas high As is found mainly inside paleosole formations and reach up to 320 mg/kg and in the metamorphosed mica-schists that were highly affected by weathering phenomena (up to 100 mg/kg). The highest concentrations of Cr and Ni are found in greenstone of the Hymettus area (396 and 105 mg/kg of Cr and Ni respectively) and serpetinised ultramafic rocks of Aigaleo (up to 3000 mg/kg for both elements).

Spider diagrams showed that there is a considerable enrichment in PHEs in the various rock types of Athens Basin compared to the upper continental crust concentrations. Also, the Index of Geoacummulation and Enrichment Factor have been estimated for selected soil-samples collected in a previous top-soil survey by setting as background values results of the present survey. A significant output of the present study is its contribution to the availability of geochemical background data in the Athens Basin concerning total concentrations of major and trace elements in various rock types. This information is particularly useful in the assessment of contaminated land as it provides a basis for comparison against the real geogenic content of the elements, enables the calculation of realistic elemental enrichment factors in soil and allows the setting of rational remediation goals in the surface environment.

ΠΕΡΙΛΗΨΗ

Αυτή η μεταπτυχιακή διατριβή παρουσιάζει τα αποτελέσματα της λιθογεωχημικής έρευνας που διεξήχθη στο Λεκανοπέδιο της Αθήνας. Συλλέχτηκαν και αναλύθηκαν 46 δείγματα πετρωμάτων. Οι συγκεντρώσεις των κύριων στοιχείων και ιχνοστοιχείων που μετρήθηκαν στα δείγματα χρησιμοποιήθηκαν προκειμένου να αξιολογηθεί η συσχέτισή τους με τους διάφορους τύπους πετρωμάτων. Επιπλέον τα αποτελέσματα της χημικής ανάλυσης χρησιμοποιήθηκαν για να διερευνηθεί η επίδραση της σύστασης των λιθολογιών στον εμπλουτισμό επιβλαβών στοιχείων στα εδάφη της Αθήνας, με ιδιαίτερη έμφαση να δίνεται στο As το οποίο κατά την διάρκεια προηγούμενης έρευνας βρέθηκε να είναι ιδιαίτερα εμπλουτισμένο στα εδάφη των Αθηνών (μέγιστη συγκέντρωση 200 mg/kg). Τα στοιχεία που προσδιορίστηκαν περιλαμβάνουν τα Si, Al, Mg, Mn, Ca, Na, Ti, Fe, P, Cr, Ni, K, Rb, Ba, Th, Pb, Nb, P, Sr, As, Sn, Co, Zn, Cu και Sb. Οι αναλύσεις πραγματοποιήθηκαν με τη χρήση φθορισμομετρίας ακτίνων X (XRF).

Οι υψηλότερες συγκεντρώσεις As εντοπίζονται στο κεντρικό και δυτικό τμήμα της λεκάνης της Αθήνας. Οι περιοχές που καταγράφονται οι υψηλότερες μέσες συγκεντρώσεις είναι στα Τουρκοβούνια, στο βόρειο-κεντρικό τμήμα της λεκάνης, και στις πλαγιές του Υμηττού στο δυτικό τμήμα της λεκάνης. Σε αυτές τις περιοχές υψηλές συγκεντρώσεις αρσενικού εντοπίζονται κυρίως μέσα παλαιοεδάφη φτάνουν μέχρι και τα 320 mg/kg καθώς και στα μεταμορφωμένα πετρώματα που επηρεάζονται κυρίως από εξωγενείς διαδικασίες (συγκεντρώσεις έως 100 mg/kg). Οι υψηλότερες συγκεντρώσεις Cr και Ni βρέθηκαν σε πρασινίτες στην περιοχή του Υμηττού (396 και 105 mg/kg Cr και Ni αντίστοιχα) και σε σερπεντινιωμένα υπερβασικά πετρώματα στο Αιγάλεω (έως τα 3000 mg/kg και για τα δύο στοιχεία).

Διαγράμματα που δημιουργήθηκαν έδειξαν ότι υπάρχει ένας σημαντικός εμπλουτισμός σε πιθανώς επιβλαβή στοιχεία στους διάφορους τύπους πετρωμάτων που συναντώνται στην λεκάνη των Αθηνών σε σύγκριση με τις συγκεντρώσεις των στοιχείων αυτών στον ανώτερο ηπειρωτικό φλοιό. Για αυτό το λόγο υπολογίστηκαν ο Δείκτης Γεω-συσσώρευσης και ο Συντελεστής Εμπλουτισμού, για επιλεγμένα δείγματα εδαφών από προηγούμενες επιφανειακές γεωχημικές διασκοπίσεις εδαφών. Ένα πολύ σημαντικό

αποτέλεσμα της έρευνας αυτής είναι η συμβολή της στον καθορισμό του γεωχημικού πλαισίου του Λεκανοπεδίου Αθηνών για τις ολικές συγκεντρώσεις κύριων στοιχείων και ιχνοστοιχείων στα διάφορα πετρώματα. Αυτή η πληροφορία είναι ιδιαίτερα σημαντική για την αξιολόγηση ρυπασμένων εδαφών καθώς θέτει το όριο της γεωγενούς προέλευσης των στοιχείων, και επιτρέπει τον ακριβή προσδιορισμό των παραγόντων εμπλουτισμού στα εδάφη για τα διάφορα στοιχεία, γεγονός το οποίο με την σειρά του οδηγεί στην ανάπτυξη ορθολογικών τρόπων αποκατάστασης του επιφανειακού περιβάλλοντος.

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CHAPTER 1 - INTRODUCTION

1.1 Rationale of research

Systematic geochemical mapping is considered to be the best available method to document changes in the levels of chemical elements in materials occurring at, or below the Earth's surface such as rock, soil, floodplain or overbank sediment, stream sediment, stream water, ground water and vegetation. Based on the media sampled, geochemical surveys can be divided into several categories. One of these categories is the lithoheochemical surveys that involve the chemical analyses of systematically collected rock samples. The rationale behind the sampling collection varies depending on the goals of each research but the final target is the construction of geochemical maps that are the principal means of presenting the spatial distribution of chemical elements and compounds.

The complexity of such geochemical surveys increases in cases where the natural environment meets the urban environment. The reason is that in such environments the number of factors that interact increases exponentially. From one side there are the naturally derived elements and from the other side the elements derived from anthropogenic activities. Deciphering the origin of each element in this specific environment is a target of prime interest. Finding the kind of relation between different elements and the chemical reactions that govern this relation is another target. The ultimate target though is not to construct this geochemical map for all elements but for these specific elements that is proved to influence in harmful ways the human health.

In order to become toxic for human health most elements need to meet specific chemical and physical parameters e.g. valence, chemical compound etc. As a result their abbreviation became potentially harmful elements (PHEs). An example of such elements is the heavy metals and the metalloids, because of their non-biodegradable nature and their tendency to accumulate in the human body (Ajmone-Marsan and Biasioli, 2010).

The local climate, geology and the geographical characteristics are regarded as the main natural factors that influence the urban environment. On the other hand, anthropogenic factors may include population and settlement patterns, use and misuse of resources which is primarily governed by the socio-economic conditions. The impacts from both these factors amend the concentration of potentially harmful elements (PHEs). The prime recipient of these elements is the urban soil.

A great number of such surveys have been conducted during the last years over the prospective accumulation of PHEs and other contaminants in soil and plants (Selinus et al., 2005; Kabata-Pendias and Mukherjee, 2007). Such a systematic geochemical soil survey was performed across Greater Athens and Piraeus, Greece from Argyraki and Kelepertzis (2014). One of the research aims was to discriminate the natural from anthropogenic sources of various PHEs. In the geochemical map of Athens urban soil, high total concentrations of various elements have been measured, which in many cases can pose a possible threat to human health. These elements include arsenic, chromium, and nickel. It was also found that a great proportion of elemental concentrations variability is controlled by local geology.

Within this frame, the rationale behind the present lithogeochemical study is to expand and enhance the results of the previous systematic soil geochemical survey by including geochemical data of near surface rocks within the Athens Basin. The scope was to examine the content of PHEs in various rock types and if possible to identify a connection between their concentration in soil and the rocks. The main research hypothesis is that PHEs showing a geogenic character in soil would display a clear association with specific rock types in the study area.

1.2 Research aim and objectives

The aim of the present research was the lithogeochemical study of various bedrock types occurring in the Athens Basin, with special emphasis to those which are typical hosts of PHEs. The specific objectives of the research were:

- to determine the geochemical characteristics of major rock-types within the Athens Basin with respect to their major and trace element content,
- to assess the geochemical associations between PHEs (e.g. As, Cr, Ni, Pb) and the examined rock-types,
- to investigate the effect of bedrock composition on the PHEs enrichment in Athens soil.

In order to reach the objectives field sampling of exposed rock was initially performed within the basin. The sampling locations cover areas from the east, west, north and central parts of the study area. Their choice was based on lithological criteria i.e. different rock-types, geodynamic evolution i.e. different Geotectonic Units (from Papanikolaou et al., 2004) and the affinity in soil samples that recorded various concentrations of PHEs (Argyraki and Kelepertzis, 2014). The samples collected span the entire spectrum of rock types met in the region of Athens.

Following the initial stage, samples were prepared in the laboratory and chemical analysis by X Ray Fluorescence (XRF) has been performed in order to determine the major, minor and trace elements in the collected samples. The analyses were performed in the Laboratory of Metallurgy, National Technical University of Athens. Powder X Ray Diffraction (XRD) was also used in order to determine the mineralogy of the samples.

All the chemical, mineralogical and statistical data, along with the field observations have been used to assess the relationships between elemental concentrations in rocks and also between elemental concentrations in specific rock types and the overlying soil by comparison with data of previous research.

A significant output of the present study is its contribution to the availability of geochemical background data in the Athens Basin concerning total concentrations of major and trace elements in various rock types. This information is particularly useful in the assessment of contaminated land as it provides a basis for comparison against the real geogenic content of the elements, enables the calculation of realistic elemental enrichment factors in soil and allows the setting of rational remediation goals in the surface environment.

1.3 The geology of Greece

The Hellenic orogenic system constitutes a tiny portion of the Alpine-Himalayan orogenic belt (Papanikolaou et al., 2004; and references therein). Its evolution and structure resulted by the convergence between North Godwana passive margin and Europe; and the subsequent subduction and accretion of oceanic and continental domains since the Mesozoic Period. Present day structure consists of three continental crust entities along with their sedimentary cover, which are separated by two suture zones. In a broader sense, Hellenides have been subdivided into the Internal and External. In each case, both oceanic and continental crust is met. The Internal Hellenides comprise the Rhodope Massif s.l., the Serbo-Macedonian Massif and the Vardar suture zone. Overlain by the Internal Hellenides; the External Hellenides comprise, from north to south or top to bottom, the Pelagonian Zone, the Pindos suture zone along with the Attico-Cycladic Massif, the Gavrovo-Tripolitza zone, the Ionian-Mani zone, the Phyllite-Quartzite Unit (Arna Unit), and Pre-Apulian platform (Paxos Zone), respectively (Figure 1.1).

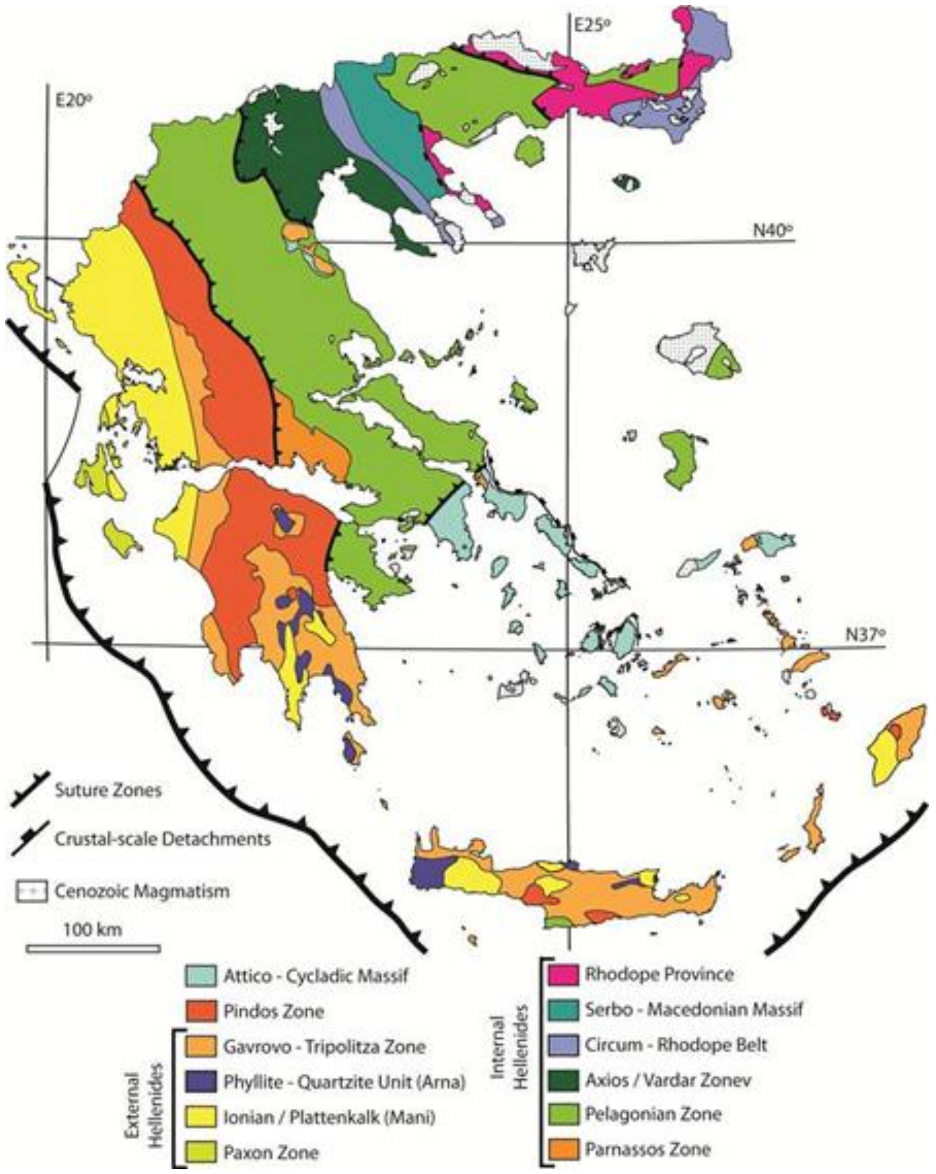


Figure 1.1. Geotectonic units of the Hellenides modified after Papanikolaou (1989), Pe-Piper and Pipper (2002), Papanikolaou *et al*. (2004), Koglin (2008) and Papanikolaou and Vassilakis (2010).

The Attico-Cycladic Massif (ACM) is a typical worldwide example of subduction zone geological environment and provides the opportunity to study processes such as subduction zone metamorphism and exhumation of HP/LT metamorphic rocks. It is exposed over a surface of about 20,000km^2 between continental Greece and Turkey, in the central Aegean Sea. With respect to tectonostratigraphy, it has been subdivided into two main structural units based on marked differences in the metamorphic and structural evolution of each one. The upper unit is consisted by various allochthonous lithologies such as ophiolite fragments, granitoids and HP-LT metamorphic rocks, as long as, post-tectonic molasse deposits (e.g. Papanikolaou, 1987; Altherr, 1994 and references therein). The lower unit is termed Cycladic Blueschist Unit, and it is in this sequence that metamorphosed HP/LT rocks are preserved in a unique way. The Cycladic Blueschist Unit (CBU) constitutes the lowest part of the Attico-Cycladic Massif overlain by a metamorphosed volcano-sedimentary sequence (Okrusch and Bröcker, 1990). The whole unit from bottom to top is constituted by three distinct piles (Philippon et al., 2012); a Hercynian basement mainly granitic orthogneisses cropping out in many islands across the Aegean Archipelago. The overlying sedimentary cover of the basement demonstrates marbles and schists, of Eocenic age (Pohl, 1999); and above this an ophiolitic mélange (Lagos et al., 2007) comprising serpentinite schists, metagabbros, jadeitites and metabasalts of oceanic origin (Seck et al., 1996). The rocks comprised in CBU, outcrop in the central Aegean Sea, southern Evia and Attica, and demonstrate HP-LT metamorphic mineral assemblages.

1.4 Geology of the study area

The Athens Basin is located in the southeast tip of mainland Greece and at the NE-edge of the Attico-Cycladic Massif. The geological formations of the broader region of Athens comprise various lithologies. The basement rocks found in Athens Basin consist of high-P metamorphic rocks making up the Hymettus and Penteli Mts., and the mountainous Lavrion area (Figure 1.2). High-P rocks are subdivided into upper and lower tectonic units (UTU and LTU; Marinos and Petraschek, 1956; Katsikatsos et al., 1986a,b; Lozios, 1993) that differ in lithology and P–T paths. The UTU was earlier exposed to erosion providing metamorphic clastic material different from that of the LTU.

According to Papanikolaou *et al.* (2004a) four geotectonic units are met in the broader Athens area and the surrounding mountains. The basement unit is comprised by metamorphic rocks, including marble, dolomite, and mica-schists.

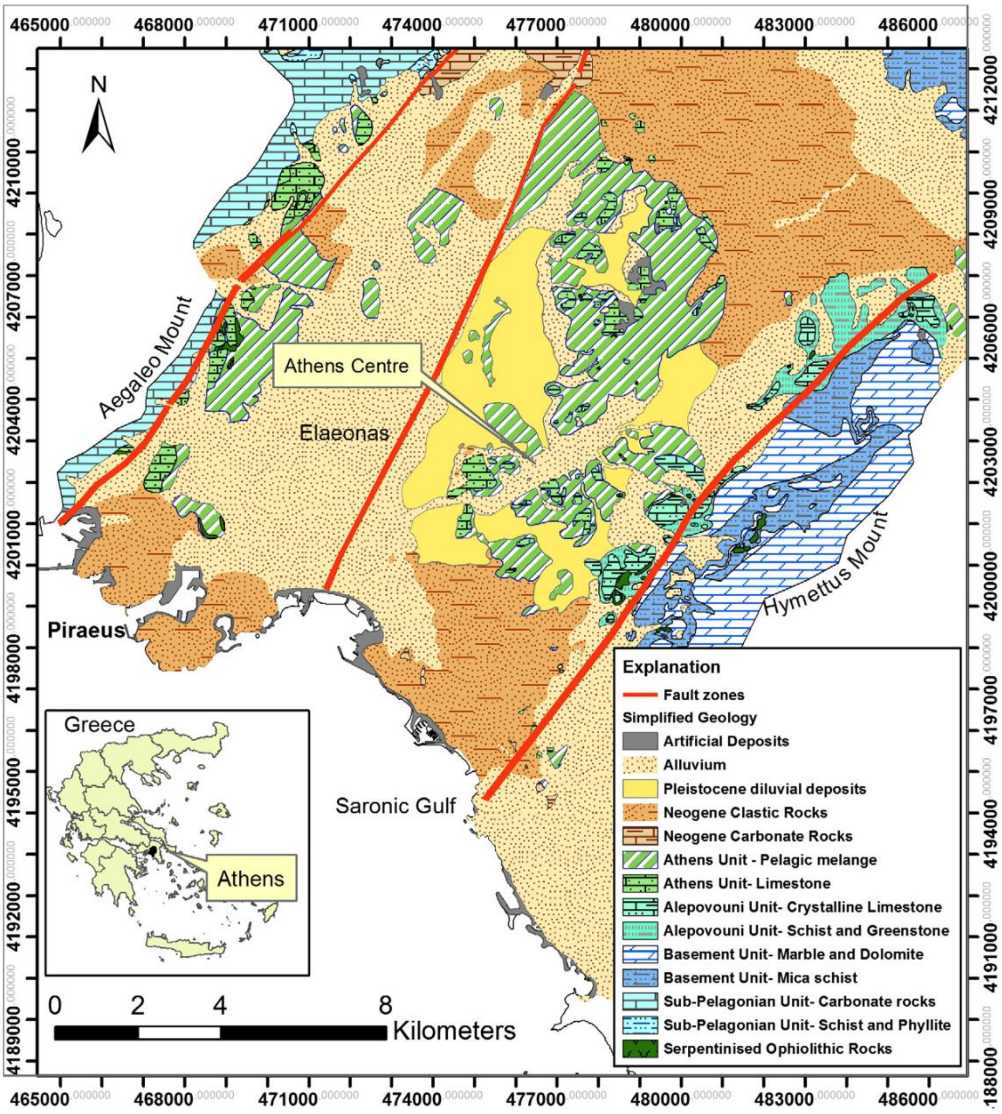


Figure 1.2. Simplified geological map of Athens Basin after Papanikolaou *et al*., (2004a), modified after Argyraki and Kelepertzis (2014)

This unit is tectonically overlain by the Alepovouni Unit that is also comprised by metamorphic rocks, including crystalline limestone, schist and greenstone; Above Alepovouni Unit lays the Athens Unit, which outcrops in the hills of western and central Athens Basin. It is an Upper Cretaceous mélange that includes pelagic sediments consisting of marly limestone, shale, sandstone, tuff and ophiolithic blocks and neritic limestone (Papanikolaou et al. 2004b). The uppermost unit is the Sub-Pelagonian, which mainly consists of limestone and dolomitic limestone. Serpentinized blocks of varying dimensions are embedded within the lithology of all alpine units occurring in Athens (Basement Unit, Athens Unit, Alepovouni Unit), not all of them are shown on the simplified geological map (Fig. 1.2). The Basement Unit and the Alepovouni Unit, which belong to the Attico-Cycladic Massif, are consisted of rocks metamorphosed in HP/LT conditions (Trotet *et al.*, 2001; Schmädicke and Will, 2003; Schumacher et al., 2008; Groppo et al., 2009, and references therein).

Post-orogenic Neogene to Quaternary deposits lie upon the aforementioned alpine lithologies. These include Neogene coastal marine, continental and lacustrine carbonate and clastic sediments, and thick Quaternary alluvial fans at the foothills of the surrounding mountains.

1.5 Geomorphology and demography of the study area

Mount Parnitha on the west, Mount Pentelikon on the northeast and Hymittos on the southeast side surround the basin. The basin's morphology is elongated with a NE-SW direction, a length of 22 km and its width reaches 11 km with a low relief compared to the surrounding mountainous regions.

The Athens Basin is dominated by urbanization as the total population over the last decades reached to a total of almost 4 million people (ELSTAT, 2013). The total area of the basin is governed by dense urbanization showing heavy traffic loads with asphalt roads and concrete-based commercial and residential buildings. These cover most of the surface in the basin of Athens. On the other hand mountainous and foothill areas hold a smaller share. Today, the urban areas of Greater Athens and Piraeus have a population of approximately 3.2 million over an area of 412 km^2. The population density (people per km^2) is approximately 7,500 and over 20,000 in a few municipalities (Fig 1.3) with a high incidence of residential, commercial, and business activities. There is no large scale industry in Athens. Some industrial support services including depots, trade transport companies and building material stocking yards are located between the Athens Centre and Piraeus. Previous industries during the past decades included pottery making, textile production, shoe making, tanneries, and metal plating.

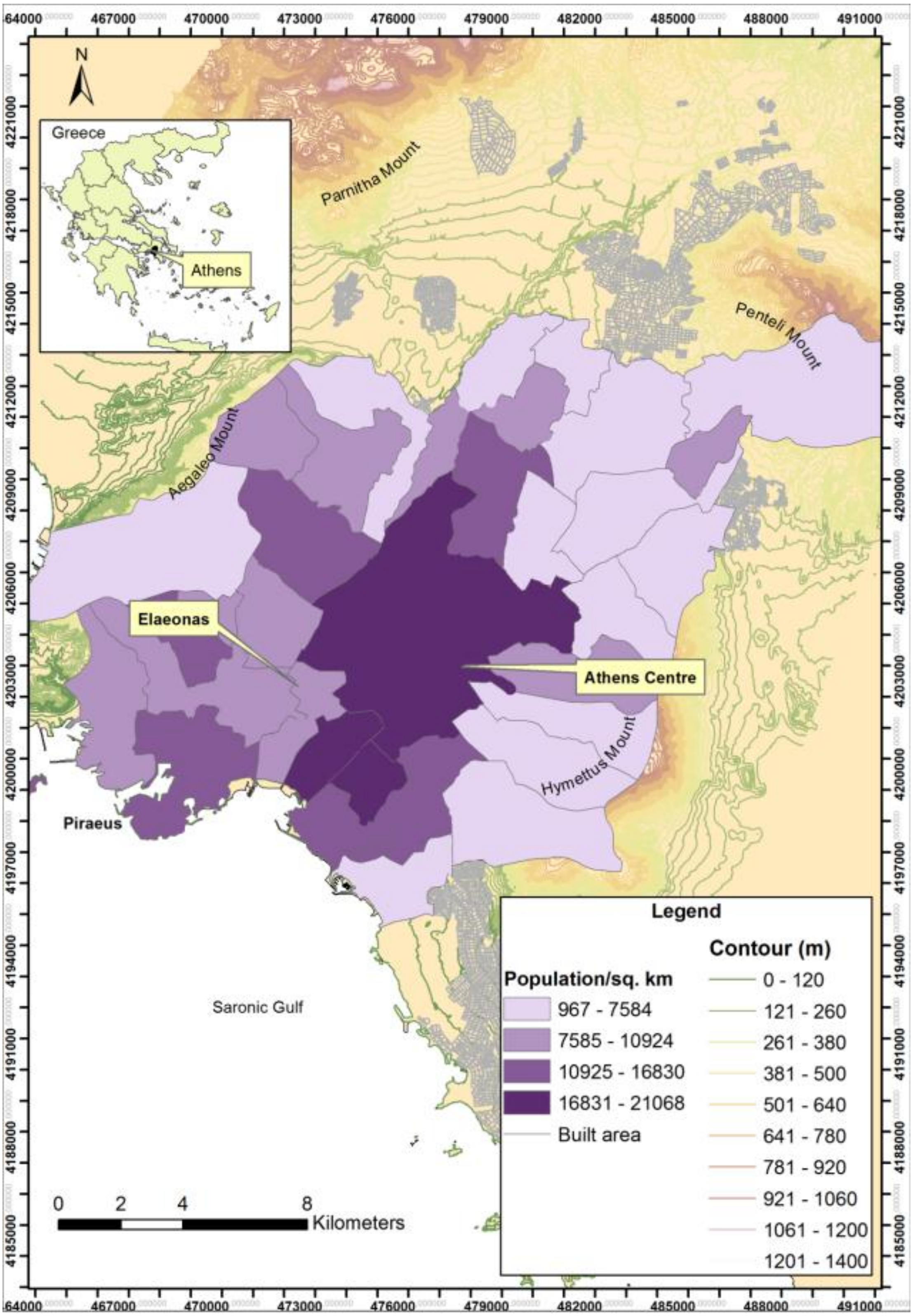


Figure 1.3. Map of the Athens Basin showing the population density data disaggregated to municipality level (Argyraki and Kelepertzis 2014).

CHAPTER 2: LITERATURE REVIEW

2.1 Lithogeochemical surveys

A lithogeochemical survey by definition is a geochemical survey that involves the systematic collection of rock samples. The derived dataset from such a survey contains the chemistry, mineralogy, petrology and geochemistry of rock samples. Goal of each survey is to provide knowledge regarding the distribution of chemical elements in the natural rock systems.

The actual target of a lithogeochemical survey depends on the type and needs of each research. As a result there are lithogeochemical surveys that are part of broader ore-exploration projects, or projects that examine the evolution of the planet from a geodynamic point of view. In our case what is of interest are the geochemical surveys that involve rock sampling and focus on research concerning environmental geochemistry. The definition of environmental geochemistry from Mackenzie (2011) is: "The impact of natural geochemical processes and human induced (anthropogenic) environmental perturbations on our natural systems (e.g. rivers, lakes, soils, forests) as well as on human health". In other words lithogeochemical surveys in environmental sciences examine the chemical parameters of rock samples that deteriorate or may deteriorate in the future the quality of the human and natural environment.

As in many other cases, lithogeochemical surveys in environmental geochemistry have a plethora of applications. The most commonly occurring one is when researchers try to establish a connection between the concentrations of an element in the soil and to discriminate its natural or anthropogenic origin. In this case one must estimate the natural background concentrations of this element. To achieve this goal lithogeochemical survey needs to be applied in the study region. This is the way of determining the natural background concentrations of an element in the soil derived by geological formations in a given region.

Taking a step back, it is important to mention that most environmental projects examine the chemical properties of soil as it is the prime recipient of hazardous elements. Most importantly though it is the most commonly occurring surface in the modern urban environments and humans interact with it every day. As a result environmental deterioration induced by naturally occurring factors or human activity is due to the accumulation of PHEs and other contaminants in soil and plants (Selinus et al., 2005; Kabata-Pendias and Mukherjee, 2007). The connection between soil and rocks comes from its generation. The development of soil is the outcome of the interaction between solid rock, climate and biological activity. As a result one of the primary factors affecting natural background concentrations of chemical elements in soil is the diversity in underlying geology (Reimann and Garret, 2005).

Coming back to lithogeochemical surveys, besides examining the influence of local geology in the distribution of major, minor and trace elements in the soil, they also assess the side effects and deterioration that these concentrations may have in the local environment. In other words they examine in a qualitative and quantitative way the amount of a given element derived by geological formations in the local environment. The reason that makes the estimation of the natural baseline concentration so important according to Matschullat et al. (2000) is that it provides a relative measure to distinguish natural elements concentrations from anthropogenically influenced concentrations in real sample collectives (Tarvainen and Kallio, 2002; Cicchella et al., 2005; Frattini et al., 2006; Albanese et al., 2007). This distinction is crucial because the limiting values (action limits) for contaminated soil may be lower than the natural concentrations (background) over wide areas (Salminen and Tarvainen, 1997). As a result and since the parent material strongly influences soil chemical properties (Palumbo et al., 2000; Salminen and Gregorauskiene, 2000; Lasheras et al., 2006), a geochemical connection and subsequently a geochemical baseline must be determined, and both of them separately for each element in geologically different regions.

Nevertheless, lithogeochemical surveys do not have as a sole purpose the estimation of the natural background concentrations. Another integral part of a lithogeochemical survey is the identification of the mineralogy and the petrology of the samples collected. Subsequently, by defining the mineralogy of the samples one can also assess the possible mineral-carriers of PHEs. In a macroscopic scale rock geochemistry can lead towards the rock-types that have high amounts of PHEs and as a result can act as possible pools of contaminants. Additionally all the fieldwork executed nowadays is documented with very high spatial resolution and accuracy with the usage of GPS. This fact can lead into geographical patterns and subsequently models that show and predict the distribution or cycle of such elements in the environment of the study region, with regard to the geochemistry of the samples mentioned before.

To sum up, lithogeochemical surveys are an indispensable part of every environmental geochemical survey as they provide crucial evidence on to the natural derivation and geochemical cycles of PHEs. A great deal of peer-reviewed information is now available on the global elemental cycle for some hazardous metal(loid) species including As, Cd, Pb, Hg, etc. (Alloway, 1995; Adriano, 2001). The concern of their pollution arises from their exchange within and through lithosphere, atmosphere, pedosphere, hydrosphere, biosphere, and anthroposphere (Kim and Kim, 1999a, 2002; Kim et al., 2002; Mandal and Suzuki, 2002; Duker et al., 2005; Khan et al., 2009).

The geochemical cycles of these elements along with natural background values are needed in order to assess the present state of the surface environment and provide guidelines and quality standards for environmental legislation and political decision-making, especially in the assessment of contaminated soils (Salminen and Tarvainen, 1997; Baize and Sterckeman, 2001).

As a result in the following chapter the influence that lithologies exert on the surficial and sub-surficial geochemical environment will be presented.

2.2 Lithological influence on the surface geochemical environment

The rapid urbanization and industrial growth that has occurred in many places around the world during the last decades has resulted in the modification of the urban chemical environment (cf. Johnson et al., 2011). A consequence of this phenomenon is the modification of the surficial geochemical environment.

But in order to demonstrate the changes happening on the surface, the distinct portions that constitute this environment must be presented.

Elements present in soil can broadly be categorised into 3 classes according to Kabata-Pendias (2011):

- as lithogenic elements, directly inherited from the parent material,
- as pedogenic elements, lithogenic in origin but subjected to pedogenic processes, and
- as anthropogenic elements, deposited into soils as direct or indirect result of human activities.

Concentration and spatial variability of lithogenic elements in soil are largely determined by their geoavailability, which refers to that portion of a chemical element's or a compound's total content in an Earth material that can be liberated to the surficial or near-surface environment through mechanical, chemical or biological processes (Plumlee, 1994).

The geoavailability of an element is related to the susceptibility and availability of its resident mineral to chemical weathering reactions (Smith and Huyck, 1999). Several studies have already shown that parent material has a strong influence on soil chemistry (e.g., Fuge et al., 1991; Palumbo et al., 2000; Salminen and Gregorauskiene, 2000; Acosta et al., 2011; Ramos-Miras et al., 2014). It is well-known also that regional geological setting is an influential determinant of soil geochemical baselines because their values depend not only on the bedrock lithology, but also on the occurrence of mineralised belts (Galán et al., 2008; Batista et al., 2013).

Although elements inherited from mineralised parent rocks are usually present in greater than background soil concentrations, they are often tightly bound to or within soil particles and have no detrimental effects on the environment and organisms (e.g., Adriano, 1986). However, lithogenic elements may be mobilised due to changing environmental conditions or changes in soil properties, leading to a sudden occurrence of harmful effects (Stigliani et al., 1991). Filho et al. (2015) during the examination of iron oxides in soils from different lithological origins concluded that the effects of parent material on soil properties are important for both well weathered soils and little-leached soils, determining their drainage, P adsorption and capacity of element accumulation. Also the relationship between distinct geomorphological region and the pH of the parent material and the pH of the plough layers has been proved in the research by Balstrøm *et al*. (2013).

In the research by Ren et al. (2015) the reflection of Cyprus geology in the soil has been proved by examining the REE patterns in soil samples. Due to the strong lithogeochemical controls, soil REE spatial patterns reflect even subtle mineralogical variations within the various Troodos ophiolite units, the location of major transform faults and other structures, and areas that have been affected by hydrothermal alteration. What actually Ren et al. (2015) proved is the similarity between the REE pattern of each bedrock formation and the soil derived from each of these formations. The main control on the distribution of REEs in the soils of Cyprus is parental geology, as observed for most other elements in the Cyprus dataset (Cohen et al., 2011). This is consistent with the results of a number of previous regional soil and sediment geochemical surveys including the low sampling density atlas of Europe for which REEs in soils and sediments are completely attributed to geological controls (Fedele et al., 2008; Sadeghi et al., 2013a). Along with other elements that display significant primary lithological variation and low chemical mobility in surface environments, soil REE concentrations have been used to map underlying parent lithologies (Halfpenny and Mazzucchelli, 1999; Mann, 2006) and other regolith-landform patterns in a number of regional soil and sediment geochemical mapping projects (Xie and Cheng, 2001; De Vos and Tarvainen, 2006; Klassen, 2009; Woodruff et al., 2009; Caritat and Cooper, 2012).

To conclude these are some of the effects that parental lithology has on the geochemistry of the surficial and sub-surficial environments. What we see is that local geology exerts and has a very tight connection to the chemical and physical properties of the adjacent environments.

Nevertheless, there is an external factor that also affects the geochemistry of the surface, and this would be weathering processes. In general, chemically resistant phases contribute to the retention of primary lithological patterns in the weathered environment (Linnen et al., 2014). But, the effects that weathering processes have on local lithologies and subsequently on the local surface environment will be analysed in the following paragraph.

2.3 Weathering processes

Weathering is a complex process comprising physical disaggregation, chemical and biological decomposition of rocks and minerals transforming complex structure minerals in simpler ones. Weathering processes involve exogenic geochemical processes of rocks and the minerals of which they are composed (decomposition, oxidation, hydration, carbonate formation, and so on) that take place in a damp climate with the participation of soil acids or in a dry (arid) climate in an alkaline medium with marked predominance of oxidation reactions. The products of weathering are primarily transported by water flows to oceans, seas, and continental reservoirs (lakes) as mechanical suspensions and true and colloidal solutions. Because of the absorptive capacity of soils and sorption of elements by clays, the compositions of solutions undergo changes; microorganisms play a large part in this process. Weathering can be broadly categorized into two separate but not independent kinds. The chemical weathering and the physical one. Inside these two classes numerous reactions take place but in most cases all these end in the same point which is:

- the weakening of resisting framework; increased susceptibility to erosive forces
- the constant change of the landform
- the production of clay minerals and development of soils.

As can be seen in the following figure (Figure 2.1) by K.A. Lemke from the University of Wisconsin, Seven Points, weathering-types are controlled after temperature and rainfall predominantly.

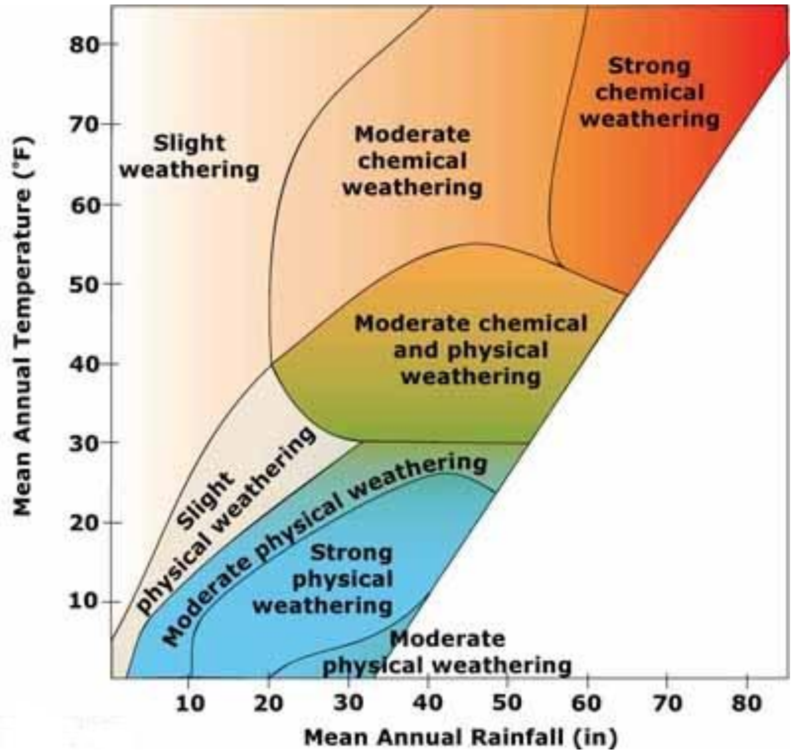


Figure 2.1. Different types of weathering mechanisms depending on the rainfall and temperature after K.A. Lemke (class lectures, University of Wisconsin, Seven Points)

What is important though to examine is the way different groups of elements and minerals respond in the weathering processes and what implications can this response have in the environment and especially arsenic.

Geoavailable metal(loid)s released from weathering of sulphide-bearing rocks and mineralised veins may be accumulated in soil through different mechanisms (Evans, 1989; Bradl, 2004), reaching concentration levels that are well beyond the normal range for unpolluted soils. Hence the importance of knowing the natural pedogeochemical background of trace elements for soil pollution assessment (Baize and Sterckeman, 2001; Bech et al., 2008; Bini et al., 2011; Wahsha et al., 2014). In the research by River *et al.* (2015) it has been showed that besides of Zn, significant inputs of lithogenic Pb, Ag, Cd, As, Sb and Tl were released by weathering from the sulphide-bearing bedrock to the surface environment. Based on their vertical distribution, most trace elements were preferentially retained in the topsoil, suggesting that metal(loid) movement down the soil profile was not well pronounced.

Pedogenic iron oxides are formed by alteration of primary minerals in the parent material or from secondary minerals. The formation and stability of these iron oxides are influenced by the diversity of pedogenetic environments under variable conditions of time, space, temperature, moisture, pH, Eh, organic matter content and ion release rate in solution (Schwertmann and Taylor, 1989; Kämpf and Curi, 2000; Bigham et al., 2002). Some intrinsic properties of minerals such as crystallinity, isomorphic substitution by aluminum (Al-substitution) and specific surface area also vary with pedoenvironmental factors such as weathering–leaching intensity, soil solution composition and drainage conditions (Motta and Kämpf, 1992; Schaefer et al., 2008; Costa et al., 2014). Moreover, iron oxy-hydroxides, with their well-documented scavenging properties (Chorover et al., 2007), can immobilize additional amounts of trace elements by adsorption processes (Rivera et al., 2015).

In the REE group we see that the general increase in REE values in soils is relative to parental lithology due to loss of mobile elements. Moreover there appear to be only limited regolith controls on REEs and other low-mobility element abundances (Ren *et al*., 2015). These results again emphasise that under typical weathering conditions, across a wide spectrum of common rock types, REEs are only weakly mobile and that secondary phases such as clays and Fe + Mn oxides are LREE-enriched due to the slightly higher mobility of the small HREE trivalent ions (Daux et al., 1994; Ridley et al., 1994). Whereas total REE concentrations generally increase, the LREE/HREE ratios increase due to the greater mobility of HREEs. This is particularly the case for carbonate rocks and the formation of terra rossa (Temur et al., 2009) as shown in the Kokkinochoria area, Cyprus (Ren *et al*., 2015). The tendency towards slightly higher ar-REE values in the top soils may relate to accumulation of REE-bearing phases in the top soil due to loss of more mobile elements and/or elutriation of REE-poor clays. The weathered profile pH does not influence REE distributions significantly until it is low enough to begin dissolving primary REE bearing phases in the original rock such as apatite and allanite (Braun et al., 1993). Because of the immobility of the REEs during weathering, the REE pattern in the soils closely reflects the geochemistry of the parental rocks, allowing mapping of subtle variations in lithology, large-scale structures and depositional environment (Ren *et al*., 2015).

Nevertheless the differences between natural and urban environments are quite few. The most important fact is the vice-versa relationship between humans and the environment in the urban areas in a variety of ways. This fact increases the complexity of the whole system. Furthermore it increases the possible implications that any possible change may have in humans' health.

2.4 Geochemical investigations in the urban environment

Focusing in urban areas we see that the urban ecosystem is a complex composite environment that is being affected by both natural and anthropogenic factors. The local climate, geology and the geographical characteristics are regarded as the main natural factors that influence the urban environment. On the other hand, anthropogenic factors may include population and settlement patterns, use and misuse of resources which is primarily governed by the socio-economic conditions. The mega-urbanization in form of increased population density, intense industrialization and excessive exploitation of natural resources characterize a megacity as a unique system but has its consequential deteriorating impacts on the overall structures and functions of the ecosystem (Antrop, 2000; Qureshi et al., 2010).

Urban soil constitutes an integral part of the city landscape, presenting unique characteristics that differentiate it from naturally developed soil. For instance, urban soil, frequently, does not present the classical vertical stratification, classified as horizons A, Band C, (Figure 2.2) and may not even reflect the mineralogical and chemical composition of the parent material (Wong et al., 2006); however, several studies highlighted the influence of natural geochemical factors on the soil chemistry even in strongly urbanized areas (e.g. Manta et al., 2002; Rodrigues et al., 2009) and the significance of geochemical anomalies in relation to lithological characteristics and human activities (Zhang, 2006; Cicchella et al., 2008; Davis et al., 2009).

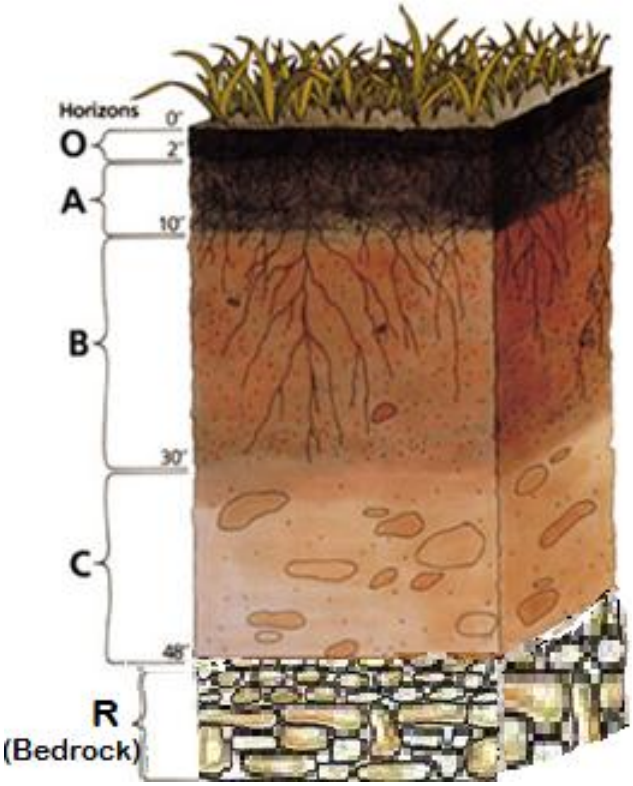


Figure 2.2. Soil profile from top to bottom a) O horizon is consisted by organic matter; b) A horizon is the surface soil; c) B horizon constitutes the subsoil and d) C horizon involves material from the parent rock

Most published urban soil investigations involve the characterization of PHEs, e.g. heavy metals and metalloids, because of their non-biodegradable nature and their tendency to accumulate in the human body (Ajmone-Marsan and Biasioli, 2010). The sources of PHEs in the urban environment can be either natural, i.e. inherited materials from the underlying parent materials (e.g., rocks, alluvium, etc.), or anthropogenic (Wong et al., 2006; Wei and Yang, 2010; Luo et al., 2012).

Despite that fact, no known lithogeochemical surveys exist with regard to environmental issues, in urban environments. The control that underlying geology exerts on soils has been well documented in a series of research studies but never in an urban environment. Towards that direction, Kampouroglou and Economou (2016), examined the possible environmental impacts of specific elements derived from lacustrine limestones in the broader region of Athens Basin, Greece. Although based only on a few samples, the later research is the first combined soil and lithogeochemical survey conducted close to a big urban centre in Greece. This fact leads us to examine the research done during the previous years in the basin where the dense-populated capital of Greece is located.

A few publications exist and these deal only with the soil geochemistry of urban areas in Attica and the wider area around Athens (Demetriades, 2010, 2011, Demetriades et al., 2010; Massas et al., 2010, 2013; Kaitantzian et al., 2013); even under these conditions, there are no published systematic geochemical maps of urban soil for any of the major Greek cities. A systematic geochemical soil survey was performed across Greater Athens and Piraeus, Greece from Argyraki and Kelepertzis (2014). This research demonstrated the significant role of local geology in controlling the variability and spatial distribution of various PHEs. Among these, As showed relatively high concentrations in surface soil, reaching about 200 mg/kg so presenting an interesting case for further study concerning its natural origin. Based on the aforementioned in the present research, specific attention was given to the distribution of arsenic in the examined samples of various rock types.

2.5 Arsenic in the environment

2.5.1 Arsenic element characteristics

As a metalloid, third-row, group V element, arsenic is seated beneath nitrogen and phosphorus in the periodic table and thus has an excess of electrons and unfilled orbitals that stabilize formal oxidation states from +5 to –3. Arsenic bonds readily to a variety of ligands, which strongly influences its chemical behavior. Compared to nitrogen and phosphorus, the potential participation of lone pair electrons and outer d orbitals in arsenic bonding stabilizes some different types of molecular configurations than are found in the lighter group elements. While arsenic can combine with many other elements to form covalent compounds, it most commonly bonds to oxygen and sulfur in nature. The ability of arsenic to shift from an electropositive state, such as in oxo-anions, to an electronegative state, as in metal arsenides, is a consequence of electron occupation of bonding and antibonding orbitals of arsenic and its myriad of ligands.

Arsenic can accumulate in soil (Voigt et al. 1996), contaminate both surface water and groundwater, and be taken up by plants and animals, thus affecting the whole food chain. The element can be derived from the parent rocks or introduced anthropogenically by industrial activities, such as the mining and processing of arsenic ore or the manufacture of arsenic chemicals, or by agriculture through various pesticides. It has significant impacts on human health and ecological systems (Fergusson, 1991; Li and Thornton, 1993; García-Sánchez and Alvarez-Ayuso, 2003; Dogan and Dogan, 2007; Figueiredo et al., 2007; Kabata-Pendias and Mukherjee, 2007).

2.5.2 Arsenic in rocks and minerals

In the Earth's crust, arsenic is found in over 200 sulfide and oxide minerals and can adsorb to mineral surfaces. The most abundant mineral form of arsenic is arsenopyrite (FeAsS) (Smedley and Kinniburgh, 2002). Arsenic minerals can be transformed after their initial formation through tectonic activity, crustal recycling, hydrothermal processes, diagenesis, and low-temperature heterogeneous phase equilibria with groundwater. Mudstones typically have the highest mean concentrations of arsenic and largest range, 3–15 mg/kg, and rhyolites, arkoses, and limestones have mean arsenic concentrations of 4.3 mg/kg, 4.1 mg/kg, and 2.6 mg/kg, respectively (Smedley and Kinniburgh, 2002).

Rudnick and Gao (2003) recommend using As values of 4.8, 3.1 and 0.2 mg/ kg for the upper, middle and lower crustal rocks respectively, supporting the preference of arsenic for an upward migration due to crustal fluid movement. According to Kabata-Pendias and Mukherjee (2007), As concentrations in the Earth’s crust range from 0.5 to 2.5 mg/kg. They also reported that the average As concentrations in mafic and acid igneous rocks are in the range of 0.5–2.5 and 1.0–2.5 mg/kg, respectively. The highest As concentrations are found in argillaceous sedimentary rocks with 5.0–13 mg/kg, with 1.0–2.5 mg/kg in calcareous sedimentary rocks and 0.5–1.2 mg/kg in sandstones. Furthermore, As-rich pyrite is common in sedimentary formations rich in organic matter, especially shale, coal and peat deposits. Therefore, it can be concluded that soils from highly altered rocks subject to metamorphic and igneous activities contained relatively high concentrations of As in the surface environment (Kwon et al., 2012). Although several studies have not been able to show any significant difference in average As content among the different types of igneous rocks, except possibly a slight enrichment in volcanic glasses (Onishi and Sandell 1955; Smedley and Kinniburgh 2002; Mandal and Suzuki 2002), a thorough survey on geochemical background of stream sediments from Campania region, Italy, proved a strong dependence of As on the underlying volcanoclastic lithologies (Albanese et al. 2007).

According to Johannesson et al. (1996) and to Smedley and Kinniburgh (2002) local geology exerts a determinant influence on As geochemical behaviour. Arsenic does not readily substitute into the structures of the major rock-forming minerals. It is found mainly as minerals where the As occurs as the anion or dianion (As_2), or the sulfarsenide anion (AsS); these anions are bonded to metals such as iron, cobalt or nickel (e.g. $FeAs_2$, FeAsS, CoAsS). It can also occur as a minor component in the relatively abundant sulphide mineral pyrite. More rarely it occurs combined with copper or silver, and there are also simple arsenic sulphide minerals such as realgar (AsS) and orpiment (As_2S_3). When these primary minerals are exposed at or near the surface of the Earth, reaction with the atmosphere and surface waters causes alteration; simple arsenic oxides or more complex phases containing various metals combined with arsenic, oxygen and other anion species are formed. A large number of 'secondary' arsenic minerals are produced in this way.

Typical concentrations in natural waters are much lower, of course, with higher levels seen in river and sea waters than in rain or lake waters. Much greater levels are found locally in waters, soils and sediments where arsenic associated with mining, smelting or other industrial activities, or with geothermal systems, can dramatically enhance concentrations (by factors of 100 to 1000, or even more) (O'Day, 2006). Although baseline As concentrations in groundwater quoted in literature vary widely, in the range of four orders of magnitude, typical background natural concentrations from different countries are between <1 and 10 μg L^{-1} (Smedley and Kinniburgh 2002; Mandal and Suzuki 2002). A great number of recent studies have linked the occurrence of the element in aquifers with regional geology and hydrogeology, the most serious contamination being in alluvial fluvial/deltaic or lacustrine plains and in intermediate to felsic volcanic rocks (Welch et al. 1988; Armienta et al. 1997; Welch et al. 2000; Acharyya 2002; Spencer 2002; Ahmed et al. 2004; Bhattacharya et al. 2004; Bundschuh et al. 2006; Rodriguez et al. 2004; Kapaj et al. 2006).

Arsenic provides a very good example of the importance of speciation in relation to toxicity. Simply put, the exact form in which the arsenic occurs dramatically affects the extent to which it is a poison for humans or other organisms. The importance of speciation in relation to toxicity also has geological relevance. The primary arsenic-bearing minerals such as the metal arsenides and sulfarsenides (arsenopyrite, etc.) are virtually non-toxic, because they are highly insoluble. Problems arise when these primary minerals break down and enter solution or form much more soluble species such as the oxides.

2.5.3 Industrial uses of Arsenic

Besides its natural origin, As in the urban environment might be correlated with its uses in various commercial products historically. Although the use of arsenic by industry has greatly declined, partly because of a much fuller appreciation of its toxicity at even low levels, it has played an important role as a component of insecticides, weed killers and wood preservatives. Historically, it was also used in pigments to colour wallpapers, paints and ceramics, and it has been used in certain specialist alloys and in glass manufacture (Vaughan, 2006).

The dominant use for arsenic has been for the manufacture of chemicals such as chromated copper arsenate (CCA) used as a wood preservative, or in fertilisers, herbicides and insecticides. Much smaller amounts have been used in the manufacture of glasses and certain nonferrous alloys, and very small amounts (a few tons) of high purity arsenic are consumed by the electronics industry for the manufacture of semiconductor materials. However, as awareness of the harmful effects of even low concentrations of arsenic in the environment has grown, consumption has been rapidly declining.

2.5.4 Arsenic contamination in Greece

In Greece, high As concentrations in groundwater have been found mainly in the northern part of the country, leading to the exposure of local population to As-contaminated drinking water (up to 130 μg L^{-1}) (Andreae et al., 1983; Froelich et al., 1985; Ballantyne and Moore, 1988; Welch et al., 1988; Mitrakas, 2001; Smedley and Kinniburgh, 2002; Mandal and Suzuki, 2002; Fytianos and Christophoridis, 2004; Katsoyiannis and Katsoyiannis, 2006; Tyrovola et al., 2006; Kelepertzis et al., 2006; Planer-Friedrich et al., 2006; Katsoyiannis et al., 2007; Aloupi et al., 2009).

High As concentrations in groundwater have been detected also in the industrial area and the suburbs of Thessaloniki (Fytianos and Christophoridis 2004; Katsoyiannis and Katsoyiannis 2006; Katsoyiannis et al. 2007), as well as in other places in the Prefecture of Thessaloniki (Fytianos and Christophoridis 2004), in the Prefecture of Chalkidiki (Tyrovola et al. 2006; Katsoyiannis et al. 2007) and in eastern Thessaly (Kelepertzis et al. 2006). Moreover, Aloupi et al. (2009) examined the occurrence of As in groundwater used for human consumption and irrigation, in stream water and sediments and in water from thermal springs in the drainage basin of Kalloni Gulf, island of Lesvos, Greece. The survey revealed enrichment in both surface and groundwater hydrological systems in the northern part of the area in association with the volcanic bedrocks, while lower As concentrations were found in the eastern part which is dominated by ophiolitic ultramafic formations.

In most of these cases, the origin of As was attributed to natural sources associated with the regional geological and hydrological background such as the reducing character of the water, its long residence time, the low water flow and a potential impact on the aquifers of the hydrothermal activity manifested in an adjacent area.

As a result, the absence of big cities, large scale industry, mining activities and intensive agriculture strongly suggests that anthropogenic sources are highly unlikely the cause of arsenic contamination of aquifers and soils. Thus, as in many other cases in Greece and all over the world, the origin of As is probably attributed to natural sources. Despite that, Johannesson et al. (1996) and Smedley and Kinniburgh (2002) pinpoint that there hasn’t been established yet a clear-cut relationship between high As in groundwater and the composition of the source rocks and aquifer materials. On the other hand, elevated As concentrations in soil and natural waters in Greece, have been linked to metamorphic rocks (Gamaletsos et al., 2013)

Such a case is the basin of Athens, where no large scale industry has been ever established in the broader region. Despite that, high concentrations of arsenic have been found in the urban soil survey by Argyraki and Kelepertzis (2014). As with other PHEs it is a valid hypothesis that regional geology exerts an important yet undefined role in the distribution of arsenic in the urban environment of Athens.

CHAPTER 3: METHODOLOGY

3.1 Rock sampling

In the present study, a judgmental sampling strategy approach has been adopted. The locations of rock samples were chosen based on the following criteria: i) outcropping rocks of the alpine rock basement of Athens, ii) specific rock types that are potentially enriched in As - e.g. the Fe-Ni laterite located in the area of Aegaleo and the ankerite rich carbonate rocks located in the western flanks of Hymettus Mt. iii) rock exposures in close proximity to soil sample locations where high concentrations of arsenic in the top-soil had been detected by Argyraki and Kelepertzis (2014)- e.g. at Tourkovounia hills located in the central to North East area of metropolitan Athens. The map of sampling locations is presented in Fig. 3.1 and their detailed description is given in the following paragraphs.

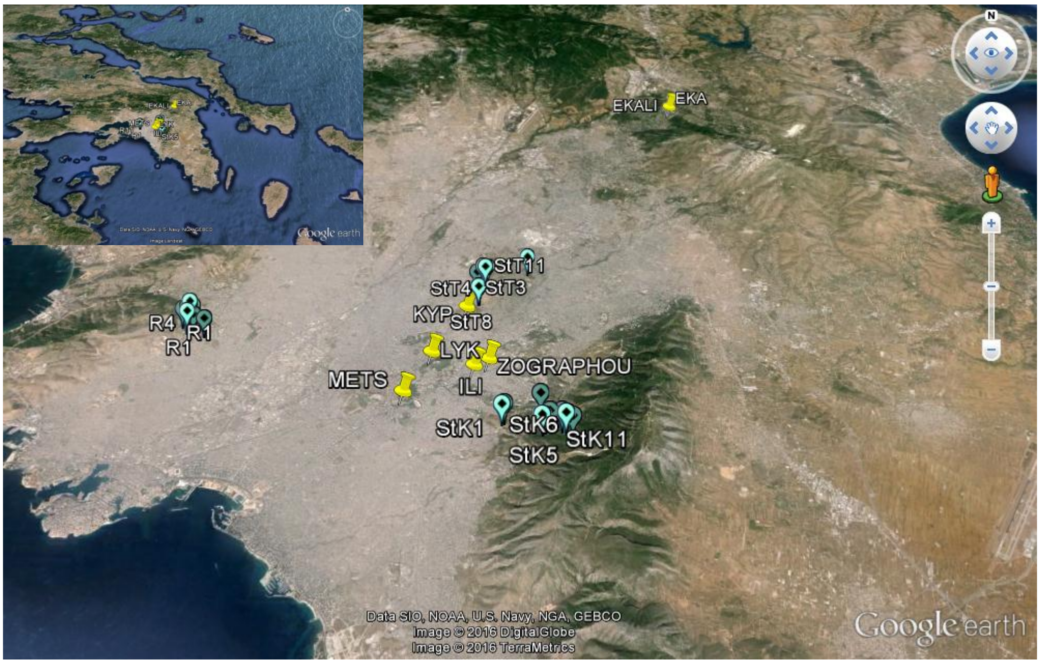


Figure 3.1. Overview of rock sampling locations within the Athens Basin.

3.1.1 Skopeftirio Hill

The dominant lithology of the hill is marble. In the foothills the marble appears affected by iron oxide zones. In the northern part of the hill close to the cemetery of Kaesariani the marble is pure with only localised evidence of oxidation (Fig. 3.2). In one case a cross-cutting vein of pure quartz has been found and collected from inside the marble sequence. In general, most oxidized carbonate rocks were found in and close to the top of the hill whereas in the lowest portions of the hill marbles were almost pure and unaltered.

Figure 3.2. Sampling locations from Skopeftirio Hill, a) pure marble, b) altered marble, c) quartz vein cross-cutting the marble sequence, d) oxidised marble

3.1.2 Hymettus western flanks

Sampling was focused in the western slopes of Hymettus Mt. close to Saketas military camp and Koutalas Hill with a northern-headed direction towards Kalopoula Hill. The lithologies met during fieldwork were mica-schist, marble and ultramafic rocks (Fig. 3.3). In a few cases quartz-veins were cross-cutting the mica-schist and the marble sequence. Where this phenomenon was present samples from both the host rock and the vein were collected. The target of this kind of sampling is to examine the spatial and chemical relation between the veins and the bedrock, and to see whether these veins are the carriers of PHEs. Oxidation phenomena have been observed in both mica-schist and marble sequences, probably due to weathering phenomena. An important observation was that inside the marble sequence the oxidation can be found predominantly into veins that cross-cut the sequence. On the other hand, the oxidation inside the mica-schist sequence can be found inside the foliation plains. In every case the oxidation is later and defines two different types of alteration-method: Through veins in the marbles and through foliation plains in the mica-schists. Moreover, inside small fractures, cracks and veins small pyrite grains have been observed, mostly within the marble sequence.

Figure 3.3. Sampling locations from Hymettus, a) highly oxidised mica-schist, b) mica-schist with intercalated quartz veins, c) marbles, d) quartz vein inside the mica schists.

3.1.3 Tourkovounia

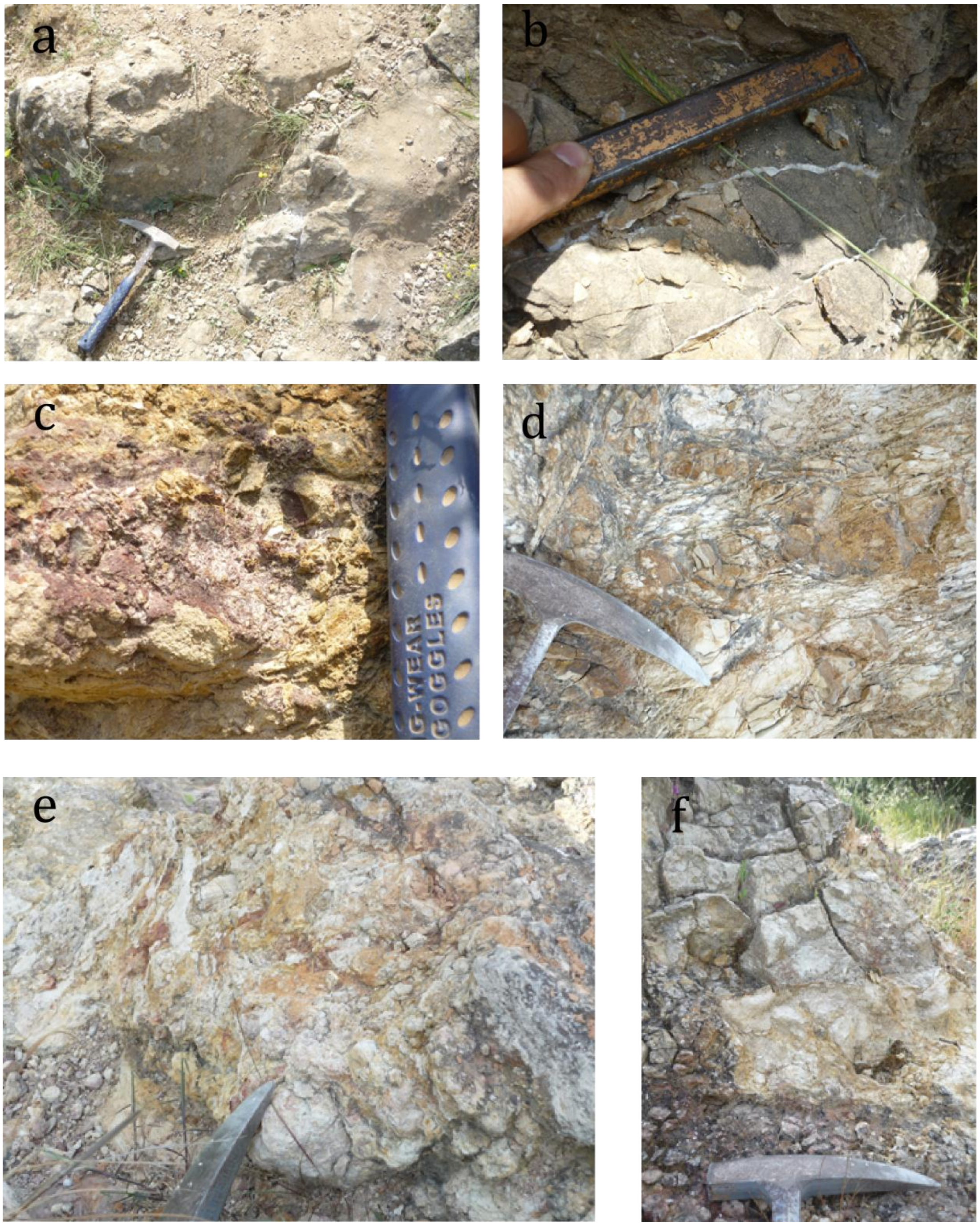
The predominant lithology of the sampling location is limestone. In some places the carbonate sequence was highly altered and oxidized probably due to weathering phenomena. These phenomena were observed locally at the top of Tourkovounia Hills whereas no indication of broad alteration or oxidation was found around the hill and especially in the side of Galatsi area. In one specific location the carbonate outcrop showed a pale yellow-brown color (Fig. 3.4, photos e and f). This formation lies in the middle of the carbonate sequence with no clear tectonic or stratigraphic transition to the limestones. Nevertheless, carbonate fragments lie inside the altered formation with an increasing abundance towards the pure limestone. This formation has been observed in another location with a smaller lateral expansion than the previous.

On the southern flanks of the Tourkovounia Hills a hydrothermal-like formation has been observed (Fig. 3.4, photos c and d). Field observations suggest a volcanic origin of the rock. The main body of the outcrop was highly sheared and weathered lying in a white mass. Inside the main body clasts and fragments of pumice-like material were found. These fragments were lighter and showed holes comparing to the ones found in pumice samples. Some purple/ dark red minerals found in hand specimen have been interpreted as hematite.

In general the whole formation looks like an altered volcanic/volcanoclastic sequence found inside the carbonate sequence. No clear correlation exists with the aforementioned altered sequence inside the carbonates as the former looks of volcanic origin.

In order to expand the handling dataset, samples from the personal collection of Assistant Prof. Athanasios Gondelitas of University of Athens have been included to the analysed samples. These samples were crystalline limestones, marbles, mica-schists and metavolcanics with a spatial span throughout the central, eastern and northern basin of Athens. Sample details and sampling locations can be found in the Appendix A (Table 1).

Figure 3.4. Various outcrops from Tourkovounia Hills, a-b) limestones, c-d) volcanic rocks, e-f) paleosole formations inside the carbonate sequence



3.1.4 Aigaleo Mountain

According to the classification by Papanikolaou et al. (2004) the Sub-Pelagonian Unit crops out in the eastern margin of the Basin of Athens in Aigaleo Mt. The lithologies met in the region are predominantly pelagic limestones of

Cretaceous age intercalated with argillaceous schists and serpentinites. All the above lithologies form a mélange-like formation. The mica- and argillaceous schists sampled from Agia Varvara area are traversed by quartz veins. Magnesite veins crosscut the serpentinite outcrops (Fig. 3.5a, b). Moreover iron-ore and chert were found in contact or inside the serpentinite bodies indicating a syngenetic evolution (Fig. 3.5c). The iron-ore (Fig. 3.5d) seemed to contain chromite crystals, an assumption that was later verified by the chemical analyses of the samples.

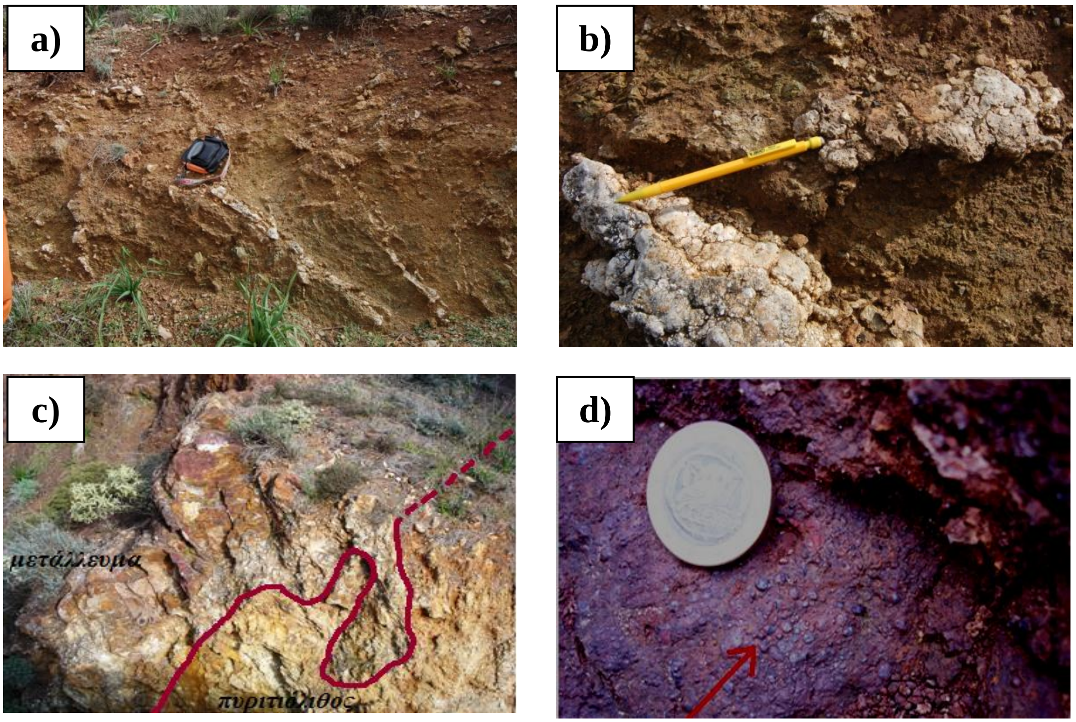


Figure 3.5. Sampling locations from Aigaleo area, a-b) magnesite veins cross-cutting serpentinite outcrops, c) Fe-ore formations in contact with cherts, d) Fe-ore formations

During fieldwork care was taken all the samples to come from unaffected by weathering processes surfaces. The samples collected ranged in weight from 3kg to 4kg. This allowed us to have enough of quantity of sample media for all the analyses conducted during the research and also backup samples in case of loss. A detailed table of all the samples collected and analysed during the present thesis can be found in the Appendix A (Table 1).

3.2 Sample preparation and analytical methods

Whole-rock powders preparation was made in the Laboratory of Economic Geology and Geochemistry at the University of Athens, Greece. The collected samples were first crushed in a steel jaw crusher and then ground in an automated tungsten carbide mortar. Eighteen major and minor oxides and a suite of 18 trace elements were determined quantitatively by X-ray fluorescence spectrometry (XRF) using a SPECTRO XEPOS ED-XRF spectrometer and the XlabPro software at the School of Mining and Metallurgical Engineering, NTUA. The SPECTRO XEPOS performs energy dispersive X-ray fluorescence analysis with polarized excitation (ED-XRF) (Fig. 3.6).

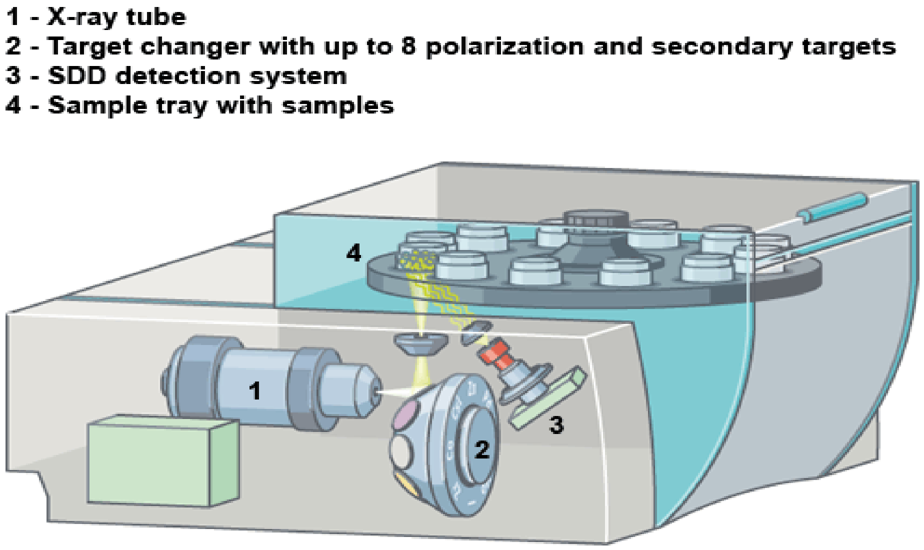


Figure 3.6. The SPECTRO XEPOS ED-XRF spectrometer with a 12- autos ampler operated at the School of Mining and Metallurgical Engineering at the National and Technical University of Athens.

The pre-installed autosampler holds 12 samples during each analysis. These twelve positions for samples vary between 32mm and 40 mm in diameter. Aliquots (14 g) of each air-dried homogenised sample were ground and formed into pressed powder discs for analysis. A series of powdered rock Certified Reference Materials (CRMs) of the Geological Survey of Japan were analysed in parallel with the collected samples for analytical quality control purposes and specifically for the estimation of analytical bias. A detailed table of the used CRMs can be found in the Appendix A (Table 1). A total of six samples (10% of the collected samples) were analysed in duplicate for the estimation of analytical precision.

Powder X ray diffraction (XRD) was used in order to identify the mineral assemblages of the collected samples. The analyses have been conducted in the Laboratory of Geochemical Investigation at the Institute of Geological and Mineral Exploration (IGME) and in the Laboratory of Economic Geology and Geochemistry, University of Athens using a Siemens D-5005 instrument. The samples were scanned in a range of angles from 3° to 65° for 45 minutes with a velocity of 1°/min. The X-Ray radiation had a wavelength of λ=1.54Å (CuKa) in a voltage of 40kv with a frequency of 40mHz. For the construction of the diagrams EVA 2.2 software has been used.

3.3 Statistical treatment and results evaluation

The concentrations of the following major and trace elements have been measured: Si, Al, Mg, Mn, Ca, Na, Ti, Fe, P, Cr, Ni and K (major elements), Rb, Ba, Th, Pb, Nb, W, La, Ce, P, Sr, Nd, Zr, Y, Ga, Mo, As, Sn, Co, Zn, Cu, S, U, Sb, Bi, Cd, Hg, Tl and Ag (trace elements).

The statistical analysis software packages Minitab and IBM-SPSS v.22 have been used for statistical analysis of the data. This included hierarchical cluster analysis and plotting of dendrograms, factor analysis and correlation analysis. Correlation was calculated between different elements in the various rock types, inside specific sampling areas and between the different petrological units met in broader Athens region. The results were also compared with available literature data from previous studies on rock and soil geochemistry within the Athens basin. The values of PHEs in Athens soil were derived from Argyraki and Kelepertzis (2014).

CHAPTER 4: RESULTS AND DISCUSSION

4.1 Sample mineralogy

The combined results of fieldwork observations and PXRD analyses are presented in the following paragraphs. PXRD diagrams are presented in Appendix B.

4.1.1 Hymettus

The rock types sampled during the field excursion involved marbles, mica schists, quartz veins intercalated inside the later rock-types. All the rock types belong to the Basement Unit met in the region of Athens (Papanikolaou et al., 2004). The mica-schists contain predominantly white mica, quartz and biotite and chlorite with some minor plagioclase. The marble sequence besides calcite which is the dominant mineral contains some small amounts of quartz, muscovite, chlorite and albite. The amount of the later increases where the quartz veins intrude the carbonate sequence. In one case, in the carbonate sequence, the sample showed dolomite as the dominant mineralogy.

4.1.2 Tourkovounia

The predominant rock-type sampled in the Tourkovounia area were paleosoles and limestone along with two samples that showed a volcanic texture. The limestone showed pure calcite mineralogy with only a tiny portion governed by quartz. The paleosole samples were found as weathered horizons inside the carbonate sequence. Their mineralogy is governed by calcite, quartz, muscovite, goethite and hematite along with some opaque minerals. The samples that showed a volcanic texture were governed by quartz, muscovite, biotite and some minor amounts of albitic plagioclase.

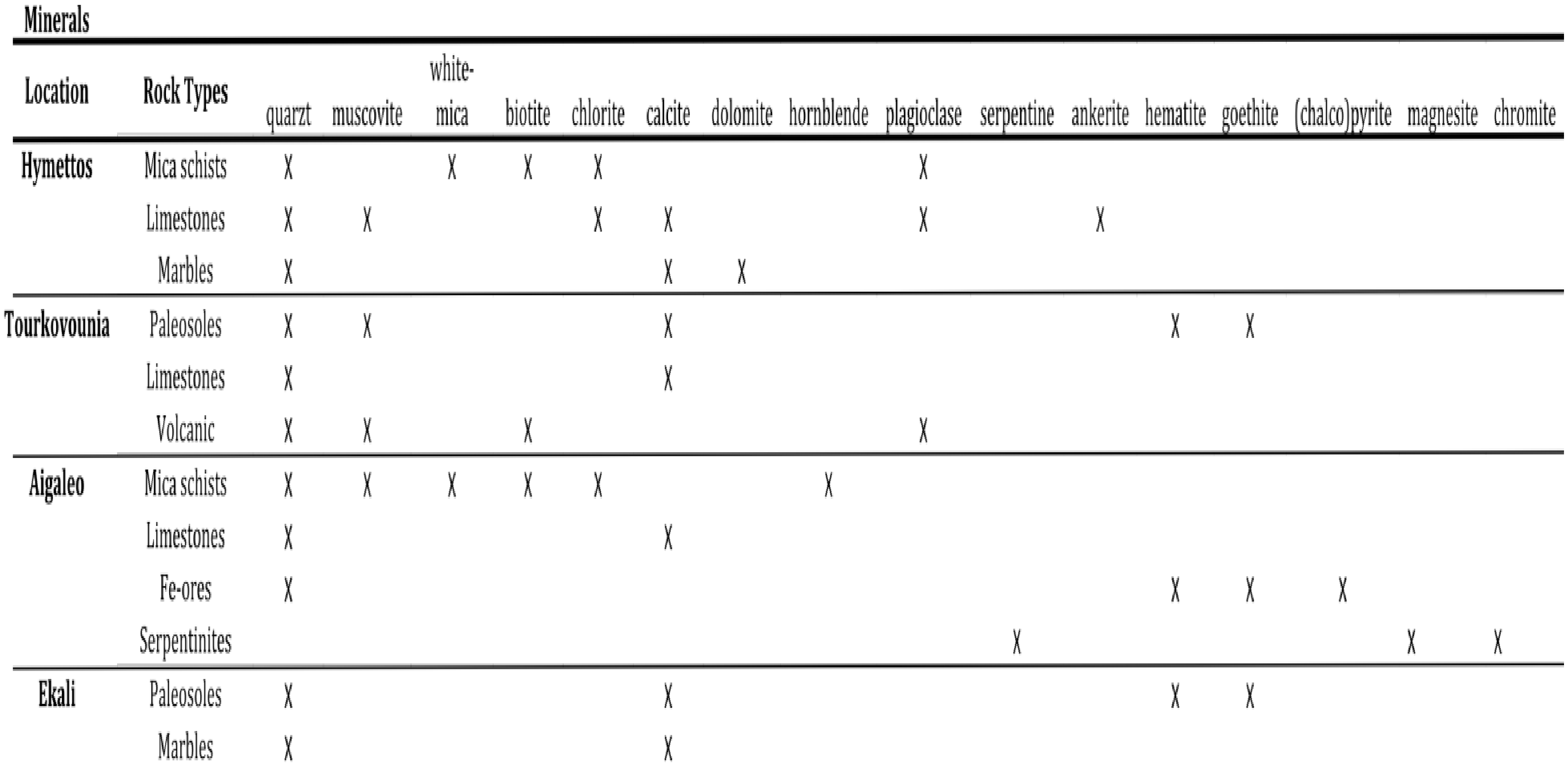
4.1.3 Aigaleo

The samples from Aigaleo involved mica-schist, limestone, serpentinite, metallic-ore samples and chert. The mineralogy of the mica-schist is dominated by white-mica, chlorite, quartz and some minor amounts of hornblende, muscovite and biotite. The limestone contains almost entirely calcite with some trace amounts of quartz. The iron-ore samples contain Fe-oxides i.e hematite and goethite and showed traces of chalcopyrite and pyrite. The serpentinite contain serpentine and magnesite inside veins penetrating the ultramafic outcrop.

4.1.4 Ekali

Two samples were collected from Ekali suburb located in the north tips of Athens urban area. The first is a marble from the same carbonate sequence as the one located in the Hymettus flanks. The marble contains predominantly calcite and some traces of quartz. The second is a paleosole formation. Like in Tourkovounia the mineralogy of the paleosole formation was a mixture of carbonate minerals i.e calcite, dolomite, quartz and metallic phases e.g. hematite.

The total mineralogical data based on the rock-type and the area of sampling can be seen in Table 4.1.



Minerals

Location	Rock Types	quarzt	muscovite	white-mica	biotite	chlorite	calcite	dolomite	hornblende	plagioclase	serpentine	ankerite	hematite	goethite	(chalco)pyrite	magnesite	chromite
Hymettos	Mica schists	X		X	X	X				X							
	Limestones	X	X			X	X			X		X					
	Marbles	X					X	X									
Tourkovounia	Paleosoles	X	X				X						X	X			
	Limestones	X					X										
	Volcanic	X	X		X					X							
Aigaleo	Mica schists	X	X	X	X	X			X								
	Limestones	X					X										
	Fe-ores	X											X	X	X		
	Serpentinites										X					X	X
Ekali	Paleosoles	X					X						X	X			
	Marbles	X					X										

Table 4.1. The mineralogy of the samples with regard to the sampling areas

4.2 Chemical analyses results

4.2.1. Analytical Quality Control Results

The analytical quality control of the chemical analysis data was based on the estimation of analytical bias by using data of the analysis of CRMs and the estimation of analytical precision by using the results of the duplicate analysis.

Estimation of Analytical Bias and detection limits

Certified Reference Materials (CRMs) from the Geological Survey of Japan have been used in order to evaluate the existence of possible analytical bias. The samples that have been used were JA-3, JB-3, JF-2, JG-3, JGb-1, JR-2 and JLs-1. The concentrations of each oxide and element (Imai et al., 1995; Imai et al., 1996) are listed in Table 4.2.

The results show that concentrations of most major and minor elements fall within ± <10% of the accepted values of the CRMs. Rotational bias has been detected for some elements with the measured concentrations deviating from the accepted values at high concentrations (Fig. 4.1). The highest rotational bias is recorded for Na, Mg and K. Smaller but yet distinct rotational bias is also recorder for Ca, Ti and Al. Silica, iron and manganese show no bias at all as there is a complete overlap between the 1:1 line and the trendline of the analyses. In the trace element group most elements show a great correlation between the measured and accepted values. Chromium shows a rotational bias in higher concentrations. Nevertheless in the case of cobalt and zircon the biases are great and so analytical data cannot be used to extract any useful information.

In XRF analyses the detection limit of most metals is 0,0001% (1ppm) and in the case of arsenic, selenium, lead and barium 0,002% (20ppm). In the cases where the amount of a specific element was below these detection limits the analysis hasn’t been taken into account.

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CRM	Accepted value	Measured Value	Bias	Bias%
Element		**Na**		
JA-3	2,37	2,8	-0,43	-15
JB-3	2,03	2,23	-0,2	-9
JF-2	1,77	2,32	-0,55	-23
JG-3	2,94	3,26	-0,32	-10
JGb-1	0,89	0,821	0,069	8
JR-2	2,96	3,41	-0,45	-13
Element		**Al**		
JA-3	8,23	7,976	0,254	3
JB-3	9,1	9,22	-0,12	-1
JF-2	9,8	8,368	1,432	17
JG-3	8,19	7,117	1,073	15
JGb-1	9,26	9,027	0,233	2
JR-2	6,73	5,7	1,03	18
JLs-1	0,011	0,0156	-0,0046	-29
Element		**Si**		
JA-3	29,11	28,26	0,85	3
JB-3	23,82	23,03	0,79	3
JF-2	30,52	27,98	2,54	9
JG-3	31,45	29,86	1,59	5
JGb-1	20,41	19,3	1,11	5
JR-2	35,38	35	0,38	1
JLs-1	0,0561	0,0776	-0,0215	-27
Element		**Ca**		
JA-3	4,46	5,157	-0,697	-13
JB-3	7	7,67	-0,67	-9
JF-2	0,06	0,095	-0,035	-36
JG-3	2,64	2,98	-0,34	-11
JGb-1	8,5	9,333	-0,833	-9
JR-2	0,36	0,4068	-0,0468	-11
JLs-1	39,3728	45,2	-5,8272	-13
Element		**Mn**		
JA-3	0,081	0,0815	-0,0005	-1
JB-3	0,137	0,135	0,002	1
JF-2	0,001	0,00144	-0,0004	-30
JG-3	0,055	0,0554	-0,0004	-1
JGb-1	0,146	0,1408	0,0052	4
JR-2	0,087	0,0911	-0,0041	-4
JLs-1	0,0016	0,00299	-0,0014	-46

Element		**Fe**		
JA-3	4,62	4,539	0,081	2
JB-3	8,27	7,814	0,456	6
JF-2	0,04	0,0545	-0,0145	-26
JG-3	2,58	2,572	0,008	0
JGb-1	10,53	10,24	0,29	3
JR-2	0,54	0,5787	-0,0387	-7
JLs-1	0,0124	0,02519	-0,0128	-50

Element		**Zn**		
JA-3	0,00677	0,00674	3E-05	0
JB-3	0,01	0,00943	0,00057	6
JF-2	0,00014	0,00008	0,00006	75
JG-3	0,00465	0,00478	-0,0001	3
JGb-1	0,0109	0,01034	0,00056	5
JR-2	0,00278	0,00275	3E-05	1
JLs-1	0,000319	0,0008	-0,0005	-60

Element		**Sr**		
JA-3	0,0287	0,02756	0,00114	4
JB-3	0,0403	0,03903	0,00127	3
JF-2	0,02	0,0191	0,0009	5
JG-3	0,0379	0,03657	0,00133	4
JGb-1	0,0327	0,03013	0,00257	8
JR-2	0,000811	0,00081	1E-06	0
JLs-1	0,0295	0,02837	0,00113	4

Table 4.2: Analytical bias based on XRF analyses of CRMs. Concentrations in ww%

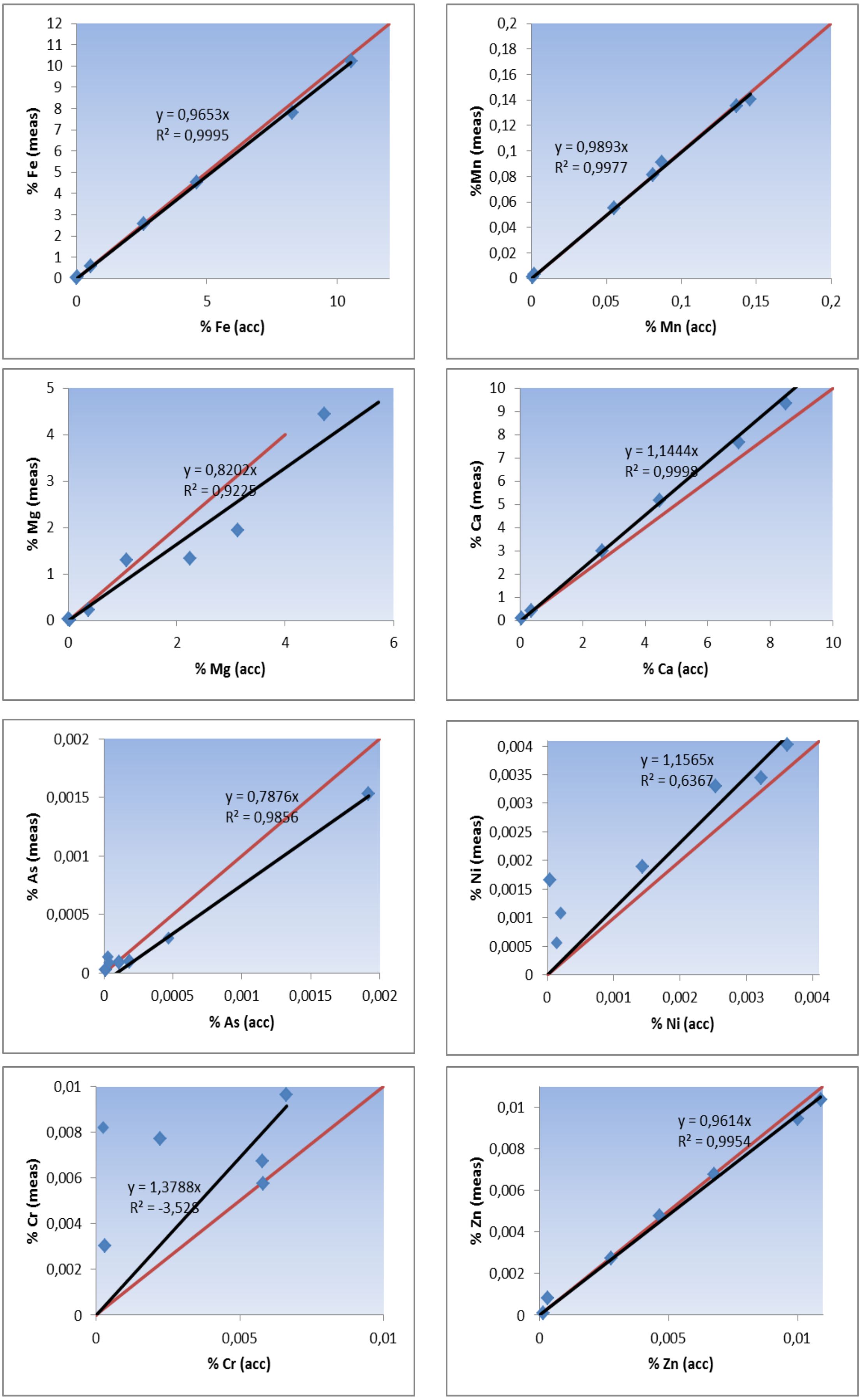


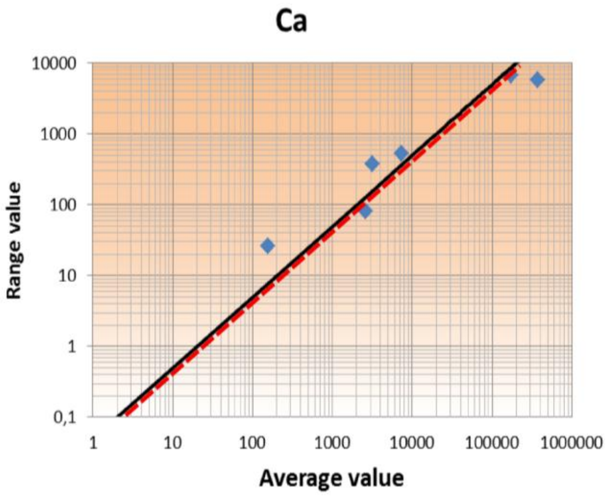
Figure 4.1: Analytical bias graphs showing rotational bias for most of the elements.

Analytical Precision

The analytical precision of the XRF analyses of the major and trace elements has been estimated by using the 10% precision diagrams according to Howard and Thomson (1978). The diagrams are presented in Fig.4.2. For the majority of the elements the precision was good to great (<±10%) at 95% confidence interval. Elements that didn't show good precision were Ba, Nb, La, Ce, U, Bi and Cd (Table 4.3).

Major Elements	Precision %	Trace Elements	Precision %
Si	3	As	10,1
Al	2,9	Cr	7,8
Ca	4,2	Zn	3
Fe	1,2	Pb	9,8
Mg	8,9	P	10,8
Mn	3	Ni	8
K	3	Sb	14
Na	10	Sr	4,8
Ti	2,6	Cu	9,8
S	7,6	V	10
		Sn	16
		Th	9,8
		Zr	1,8
		Rb	4

Table 4.3: Percent of analytical precision for major and trace elements based on 6 duplicate analyses of rock samples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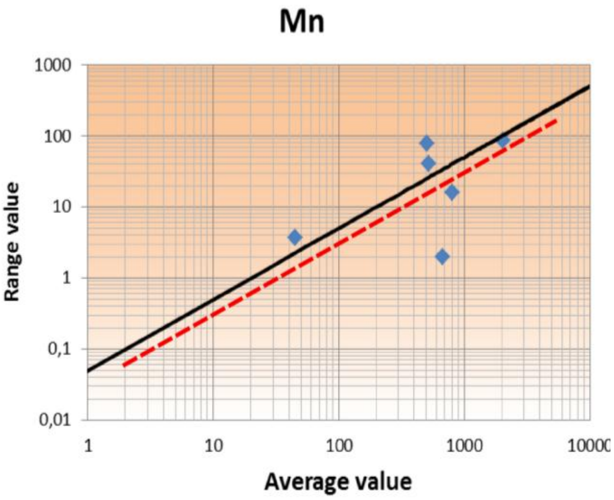
1
10
100
1000
10000
100000
1000000
Average value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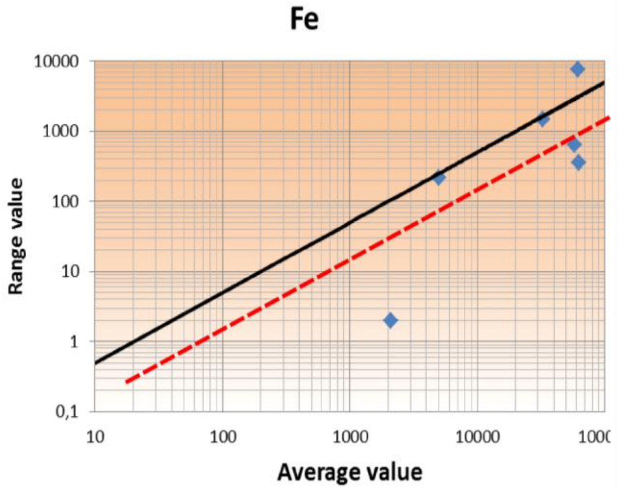
0,01
1
10
100
1000
10000
Average value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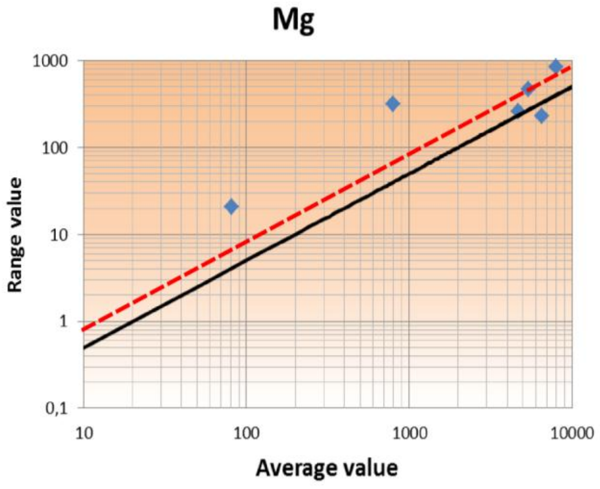
10
100
1000
10000
1000
Average value


Mg
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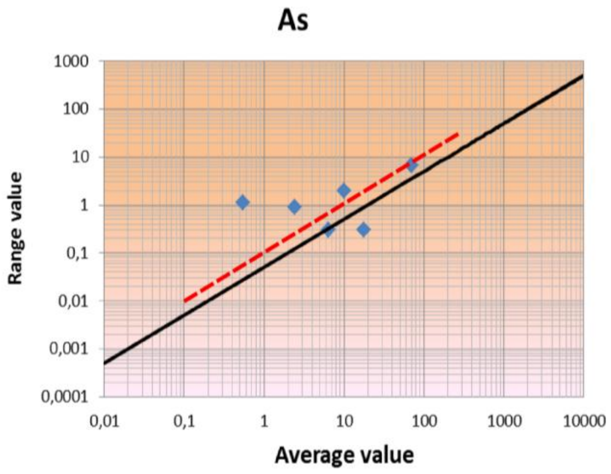
0,1
10
100
1000
10000
Average value


As
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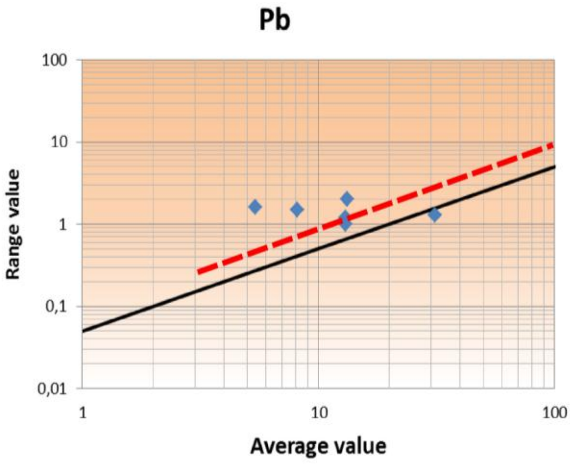
0,1
0,01
0,001
0,0001
0,01
0,1
1
10
100
1000
10000
Average value


Pb
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10
1
0,1
0,01
1
10
100
Average value

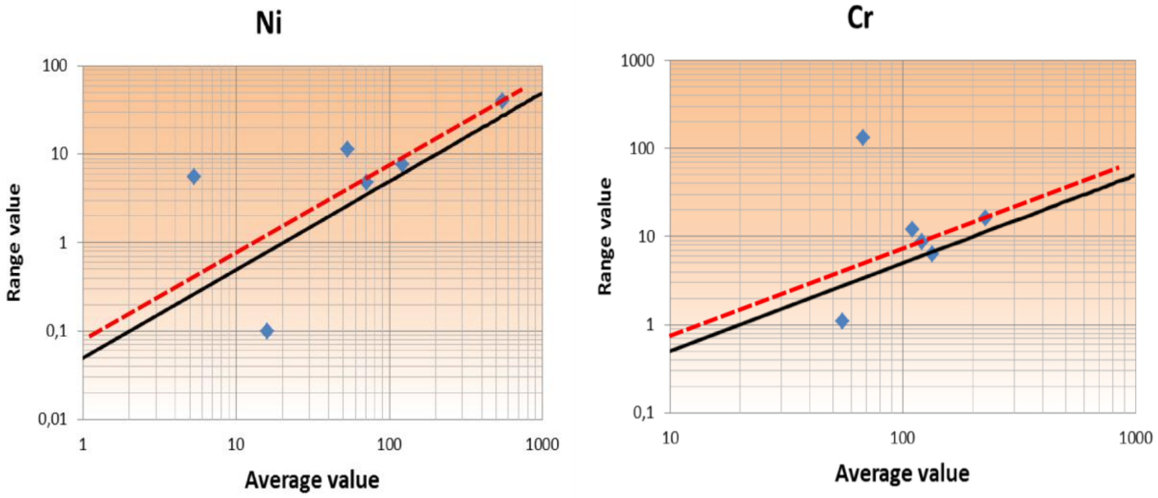

Figure 4.2.: Diagrams showing the 10%precision lines for major and minor elements. All the analyses are in mg/kg concentrations.

In summary the analytical quality control showed that some elements from the initial data package cannot be used to extract useful information and interpretations. Moreover some elements have been excluded from the stage of statistical analysis. These elements are Ba, Th, Mo, Bi, Cd, La, Ag, Hg, Tl, Ce, U, Co and Zr. The elements that passed the QA/QC and are used for further statistical analysis are Si, Al, Mg, Mn, Fe, K, Ca, Na, P and Ti from the major elements and As, Pb, Cu, Ni, Cr, V, Rb, Sb, Sn, S, Y, Ga, Zn and Sr from the trace elements.

4.2.2 Statistical Analysis

During the initial stage of the statistical analysis simple and clustered boxplots have been created in order to visually display the descriptive statistics of the data. Another parameter that has been inserted in these plots is the lithological unit that each rock type and subsequently each element belong to according to the classification by Papanikolaou et al. (2004). The Units that are present in the basin of Athens are structurally from bottom to top:

- the Basement Unit,
- the Athens Unit and
- the Sub-Pelagonian Unit

The samples collected from the eastern flanks of Hymettus Mt. belong to the Basement Unit and they comprise metamorphosed formations i.e. marbles and mica-schists. Limestones, paleosoles and volcanic rocks sampled by Tourkovounia Hills belong to the Athens Unit (Papanikolaou et al., 2004). The samples from Aigaleo area are part of the Sub-Pelagonian nappe (Papanikolaou et al., 2004). The sampling collection involved two samples collected from Ekali area in the north-west tips of Athens. These also belong to the basement unit.

The boxplots that have been created investigate the relation of specific pairs of elements as analysed in the previous chapter in comparison to the lithological units mentioned before and the various rock types. Simple boxplots examine the distribution of specific elements. Clustered boxplots examine the distribution of distinct elements and of pairs of elements among the Units, the different sampling areas and the various rock types.

With respect to the special focus of the research on As concentrations, the highest concentrations of this element were found in the samples collected from Hymettus and Tourkovounia areas (Figure 4.3). As a result the following plots created were targeting mainly these two areas.

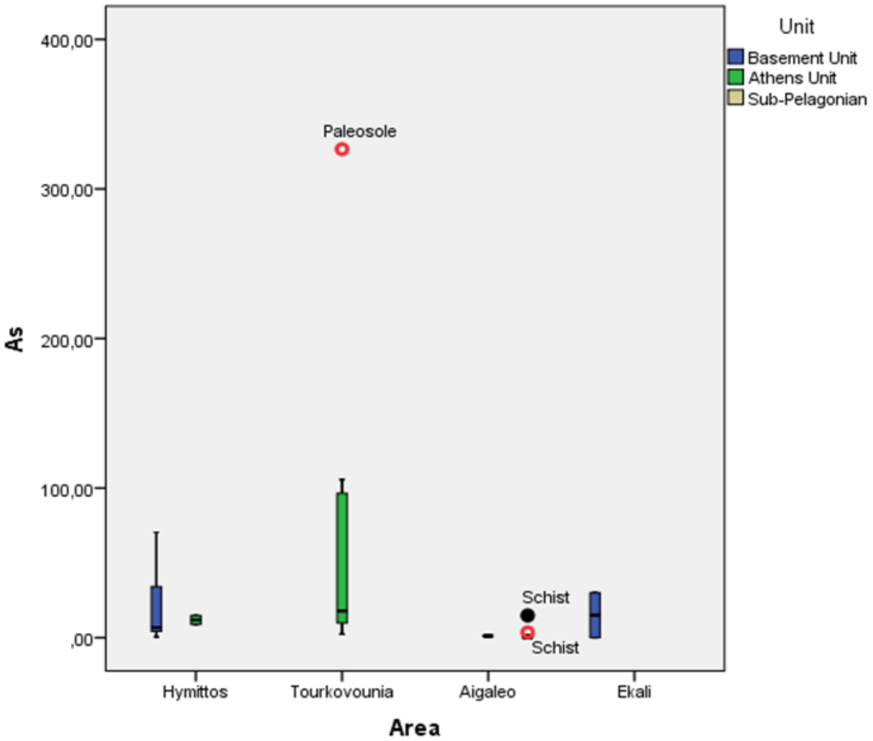

Figure 4.3: Boxplot showing the content of As in the sampling areas in comparison to the Geotectonic Units met in these areas

The boxplot presented above indicates that the highest average concentrations of arsenic in rocks are located in the central and eastern parts of Athens Basin. Plotting the various lithologies versus the Geotectonic Units met in the broader region of Athens showed that the Basement Unit and the Athens Unit have the highest amounts of arsenic (Figure 4.4). The same spatial distribution with arsenic among the different areas and units shows antimony and copper in Tourkovounia Hills and Hymittos area in respect.

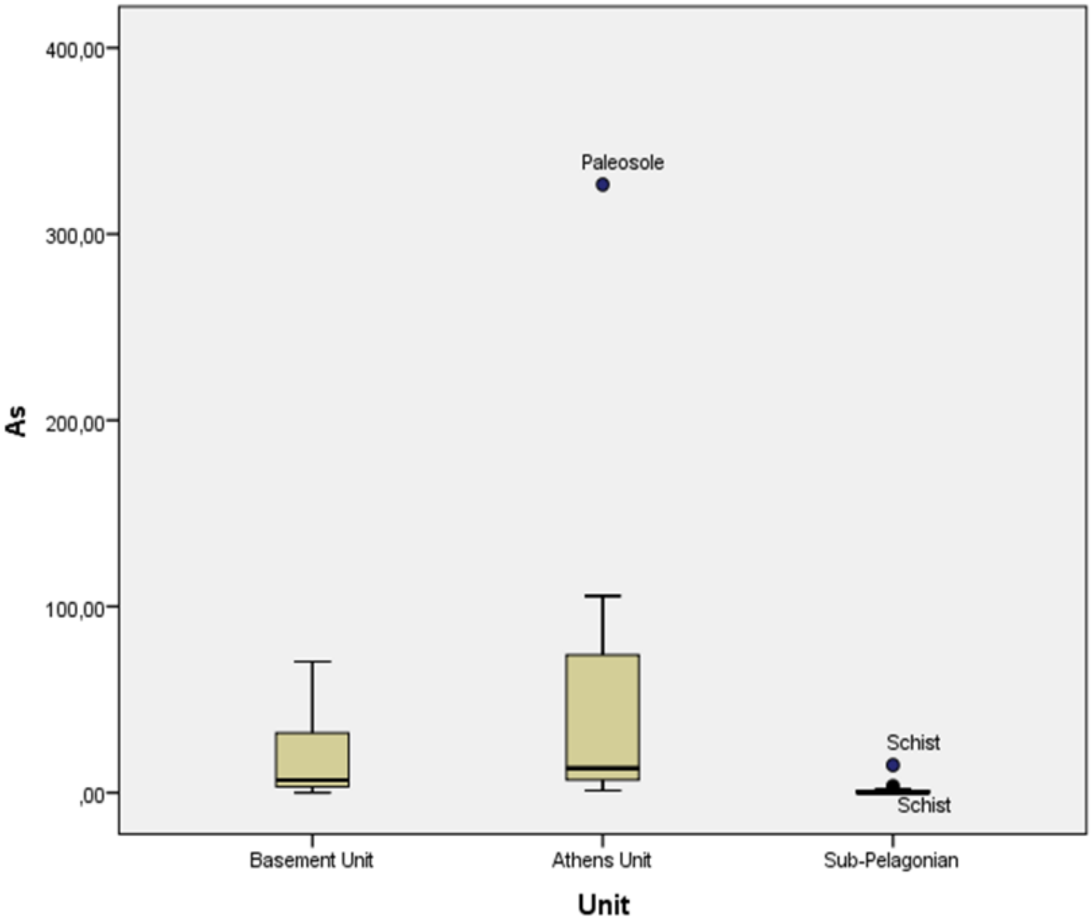

Figure 4.4: Boxplot showing the As content in the various Geotectonic Units of Athens in comparison to the various lithologies

In the samples from Hymittos, arsenic showed a good correlation with copper (Figure 4.5). The boxplot created reveals a disproportionate relation that these elements have for Hymettos and Tourkovounia areas in respect.

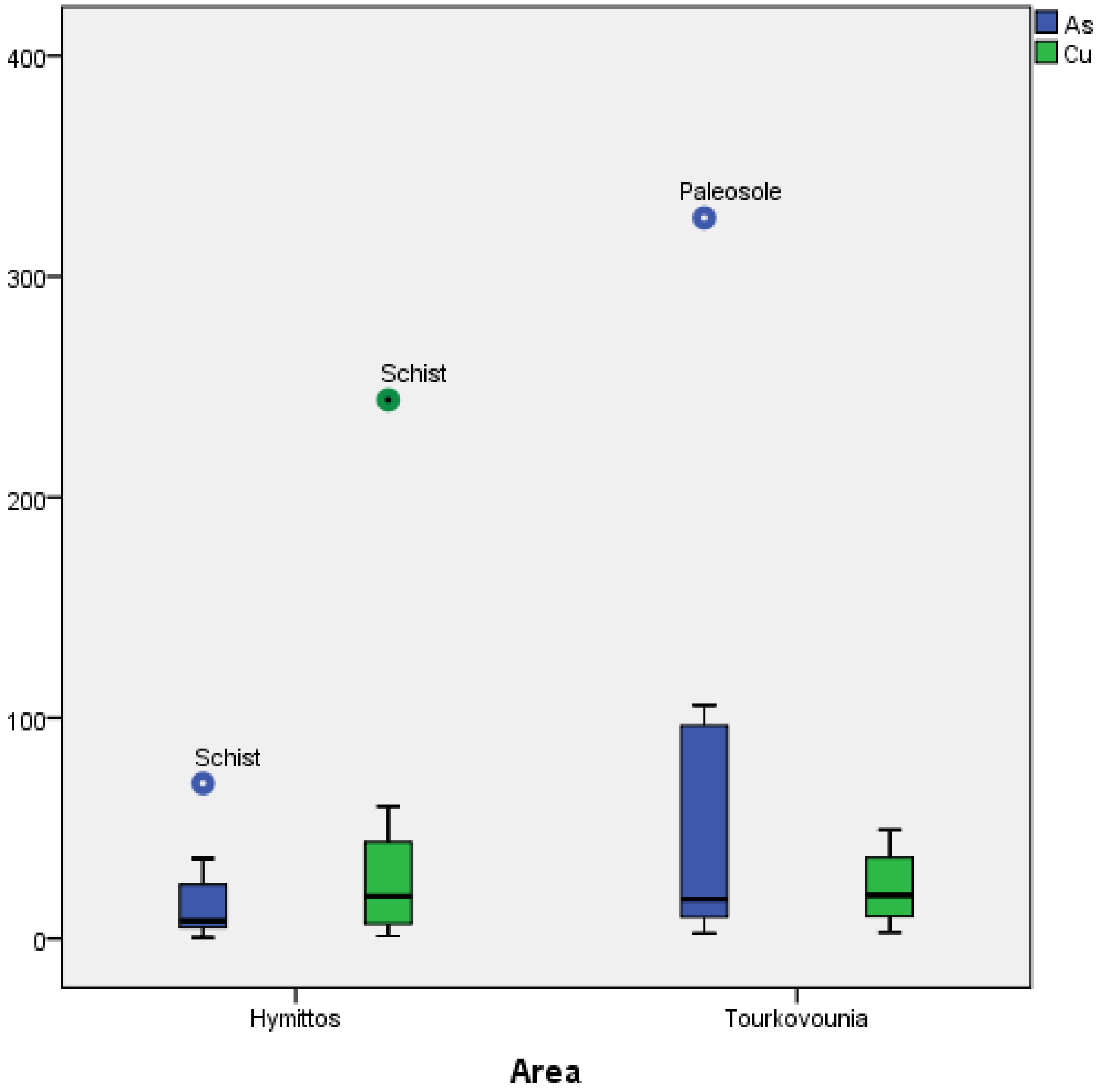

Figure 4.5: Boxplot depicting the content of As and Cu in the sample areas

Two boxplots have been created concerning Sb in order to examine its relation with arsenic. These boxplots correlate the content of Sb in comparison to the sampling areas (Figure 4.6) and the Geotectonic Units (Figure 4.7) and both these with regard to the various lithologies.

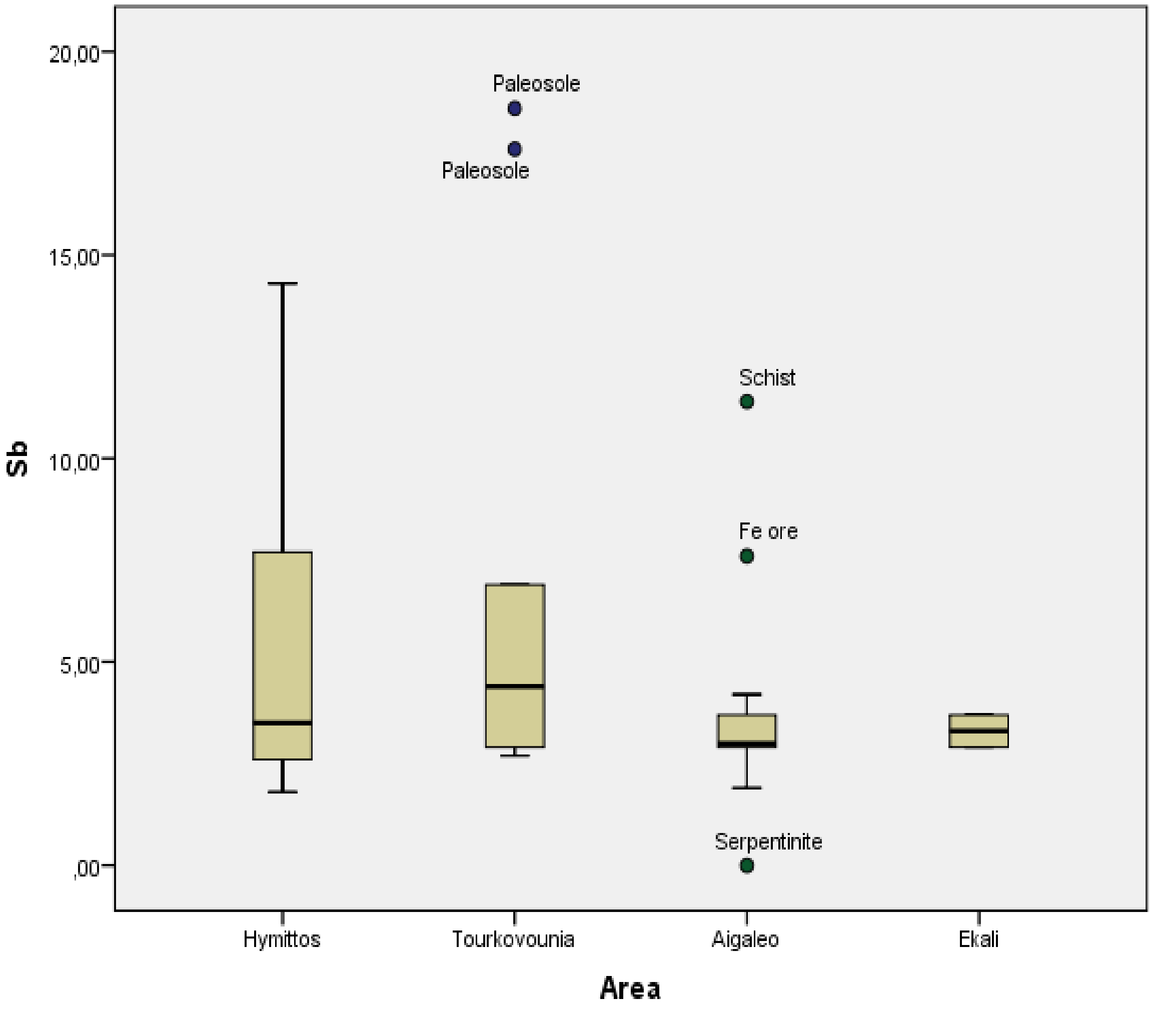

Figure 4.6: Boxplot depicting the distribution of antimony among the different areas .

The above boxplot shows that Sb records the same dispersion with As and especially in Tourkovounia area where it records the smallest error range.

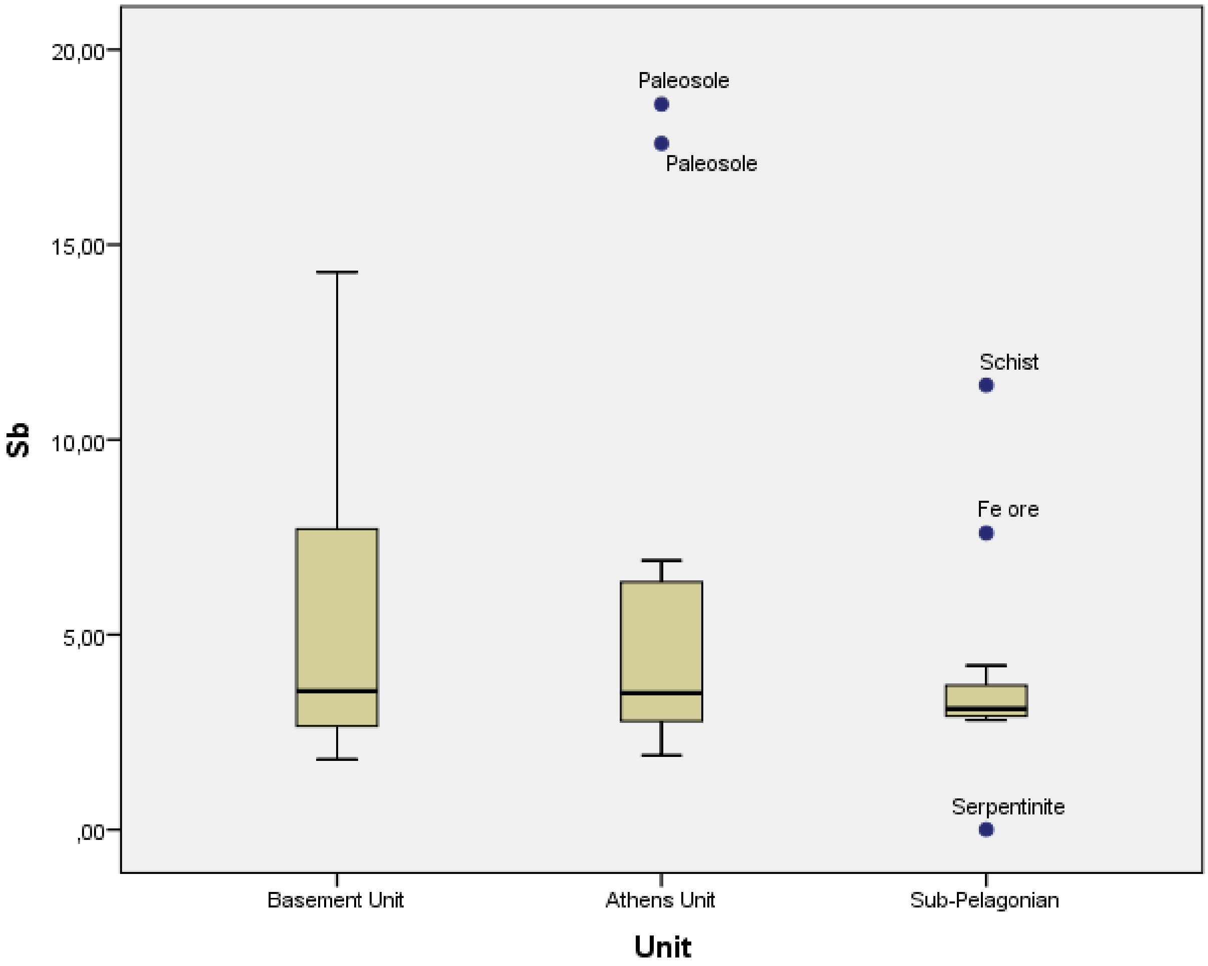

Figure 4.7: Boxplot showing the distribution of Sb among the different Geotectonic Units.

The above boxplot shows that Sb records the same dispersion with As in the various Geotectonic Units of Athens, predominantly in Athens Unit. The interesting thing though is that Athens Units mainly crops in Tourkovounia Hills.

4.2.1.1. Dendrograms

Following that step, several dendrograms were created with Minitab Software. The initial diagrams show the relation between major elements and trace elements and a combination of both in the whole data package regardless the area or the rock type. After that, dendrograms for each distinct region have been created. The later include Hymettus, Tourkovounia and Aigaleo sampling locations. The target was to examine the possible relations between the analysed elements. Additionally different diagrams for each distinct sampling area have been constructed in order to assess how the spatial relation between the elements changes from one to region to another.

The dendrograms designed for the whole set of the analyses indicate strong correlations between the major elements and also some distinct correlations between some trace elements. The correlations between the major elements pinpoint the various lithological rock types met in each distinct sampling area i.e. mica-schists, carbonates, ultramafic rocks, paleosoles etc. (Figure 4.8)

More accurately, the cluster that contains the alkalis i.e. potassium, aluminum and sodium is correlated with silica. This chemistry comprises the mica-schists and argillaceous schists collected from Hymettus and Aigaleo areas. Silica, manganese and iron from the major elements along with chromium, nickel, zinc and copper from the trace elements, comprise another cluster that depicts the ultramafic lithologies met in Aigaleo region. Additionally the existence of chromite grains inside the iron-ores collected in Aigaleo region is illustrated by the cluster between iron and chromium. Lead is correlated with all the rock-types but the carbonates which show their own distinct clusters. These are highlighted by the relation of calcium with arsenic and antimony. The later relation has been observed in the paleosol formations sampled from Tourkovounia and Ekali region. Magnesium forms a quite clear-cut cluster. It is related with almost all the lithologies sampled. In the carbonates is found as dolomite inside the (dolomitic-) marbles and as ankerite and mica inside the limestones. The later lithologies have been observed in the broader Hymettus area. The relation of magnesium with the

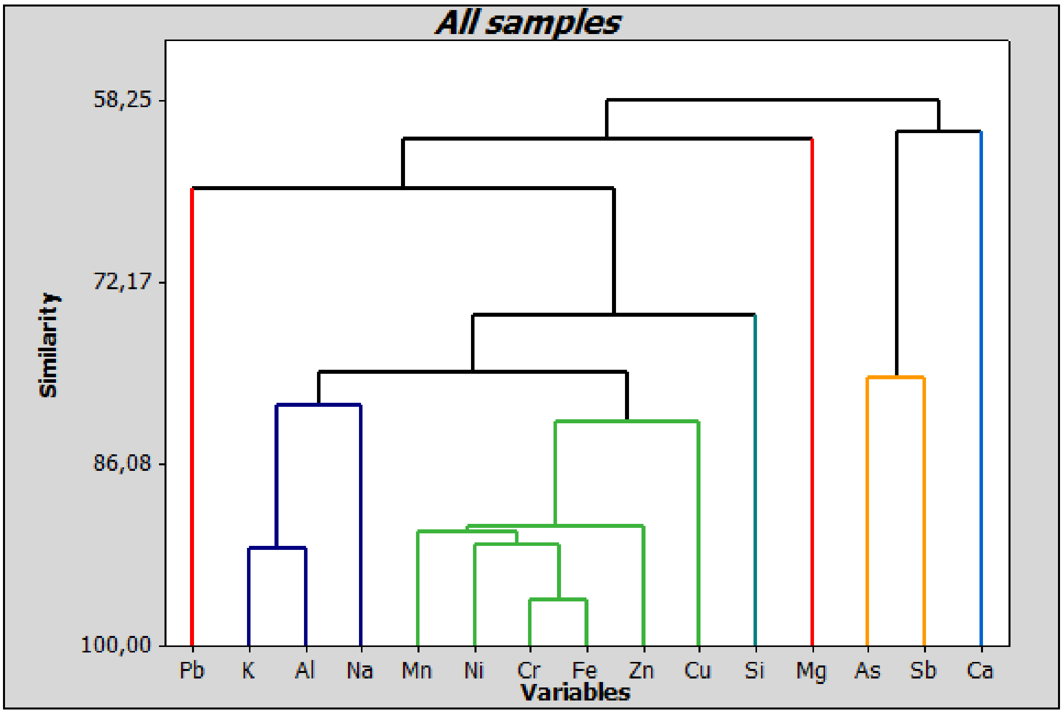

Figure 4.8: Dendrogram containing all samples regardless of sampling area

alkalis is coming from the schists sampled from Hymettus and Aigaleo areas. Again the presence of micas such as muscovite and biotite along with plagioclase prove this correlation.

The relations between the major elements do not vary significantly between the different sampling locations. In the trace elements though these relations change dramatically as we will see further below.

-Hymettus

The samples collected by Hymettus Mt. involved mica-schists, marbles and dolomites. The dendrograms for the major elements depict the rock types met in the area. As for the trace elements, there is a strong correlation between arsenic and manganese and both these with zinc and copper. The relation between the major and trace elements will be analysed further below with regard to the lithologies and the chemical analyses of the samples (Figure 4.9).

The major elements form 3 distinct clusters. Calcium shows a strong relation with magnesium which can be attributed to the dolomites outcropping in the area. Magnesium is also correlated with silica. The presence of pure marbles is responsible for this relation. The third cluster combines silica and magnesium with the alkalis and iron. The later chemistry is found predominantly in the mica-schists. As for the trace elements arsenic shows a distinct relation with manganese. These two elements are found inside the mica schists samples and especially to those that weathering processes affected the outcrops with great intense. As a result their correlation can be attributed to supergene reactions triggered by weathering. Arsenic and manganese are both correlated with zinc and copper. These two show the highest concentrations in the mica-schists with a decreasing amount, though still high, in the marbles. What must be noted here is that the amount of zinc in the samples remains constantly high whereas copper decreases especially in marbles. So it seems that these two elements despite their presence in the same samples do not have the same behavior with regard to their concentrations. Additionally lead and sulfur showed no worthy relations between other elements. What can be mentioned here is the constant though low amounts of lead in all the samples collected from this area and.

Another relation worth mentioned is the one between zinc and copper. Both elements record the highest concentrations in this area. The average concentration for zinc reaches up to 73 mg/kg.

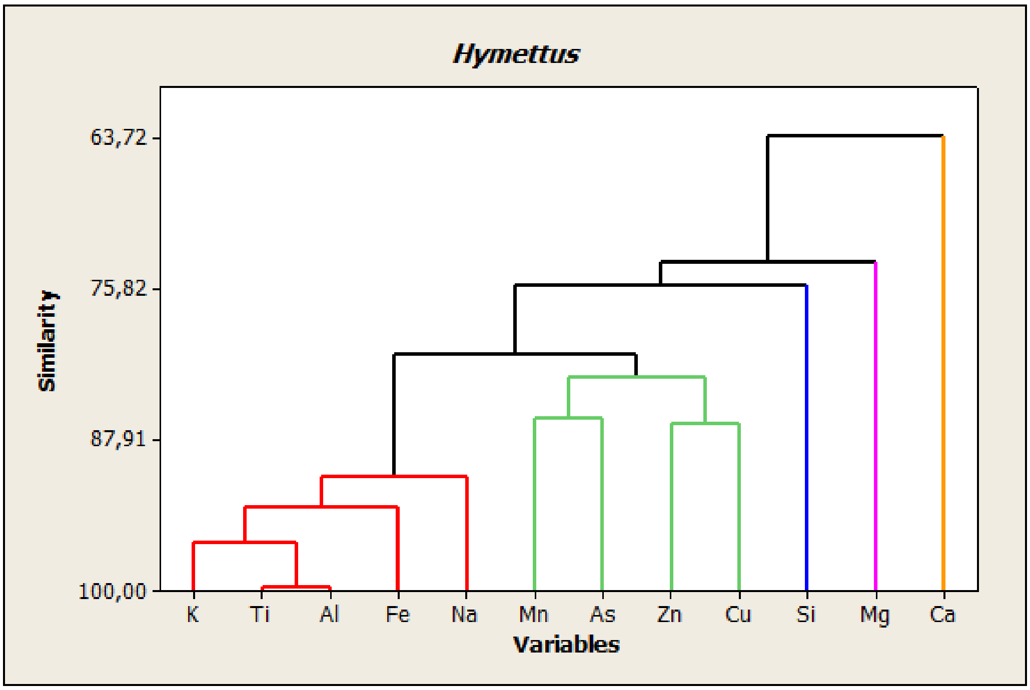

Figure 4.9: Dendrogram depicting the relation of major and minor elements for the samples from Hymettus area

- Tourkovounia

The samples collected from Tourkovounia hills comprise limestones, paleosoles and volcanic rocks. Again the dominant rock types can be distinguished by the relations between the major elements. On the other hand, the trace element patterns and relations change radically from the ones in Hymettus area. The results will be analysed with regard to the chemical, mineralogical and statistical analysis.

Again the major elements form two distinct clusters that represent the dominant rock types. The first cluster contains calcium that depicts the limestone samples collected. The second cluster depicts the volcanic sequence and comprises iron, manganese, magnesium, silica and alumina. The third major rock type, paleosoles, is represented by the same cluster with the limestones but in this case arsenic and antimony come along. The later correlation can be explained in terms of field relations. The paleosoles are formed inside joints and cracks in the carbonate sequence. As a result and based on the mineralogy of the samples which is dominated by calcite and various iron-oxides, this affinity is quite normal.

In the trace element dendrograms 3 groups are formed. The first involves lead which forms an isolate group in the first dendrogram (Figure 4.10). In the second dendrogram (Figure 4.11), that contains only trace elements, lead is showing a strong relation with nickel and chromium. The later relation is found inside the volcanic samples. Nonetheless the mineralogical analysis showed no minerals that contain lead. Despite that, the concentrations of the element in this area are higher compared to the other sampling areas.

The second group contains, as mentioned before, arsenic and antimony. These elements are correlated with calcium from the major elements group and tin and sulfur from the trace elements group. The relation with calcium has been attributed to the formation of paleosoles inside the limestones sequence. In this case it is that arsenic and antimony record the highest concentrations among all samples which in the case of arsenic reach up to 320ppm. The relation with tin has been discarded due to the low concentrations of the element in the samples. The relation with sulfur needs to be examined. This relation probably indicates the existence of gypsum but the mineralogical examination showed none. Nevertheless the rock-types found in the broader region i.e. paleosoles, volcanic rocks and limestones can be affected by weathering processes (e.g. acid rain) and create gypsum. The third group contains copper and zinc. Their affinity is restricted to the volcanic samples. Both elements record relatively high amounts.

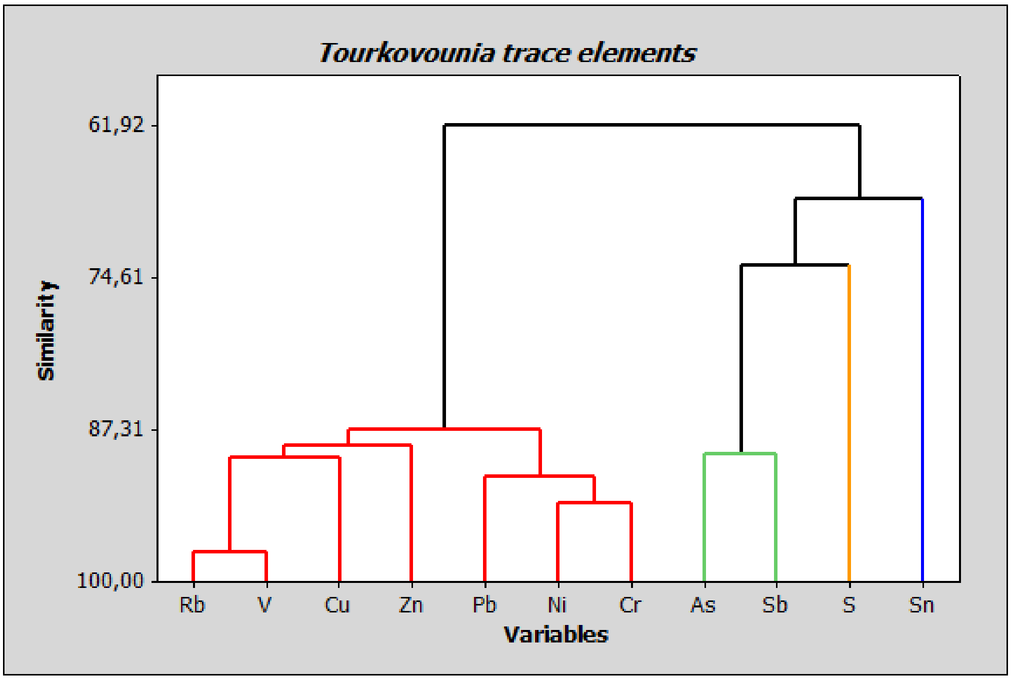

Figure 4.10: Dendrogram showing the trace elements from the Tourkovounia region

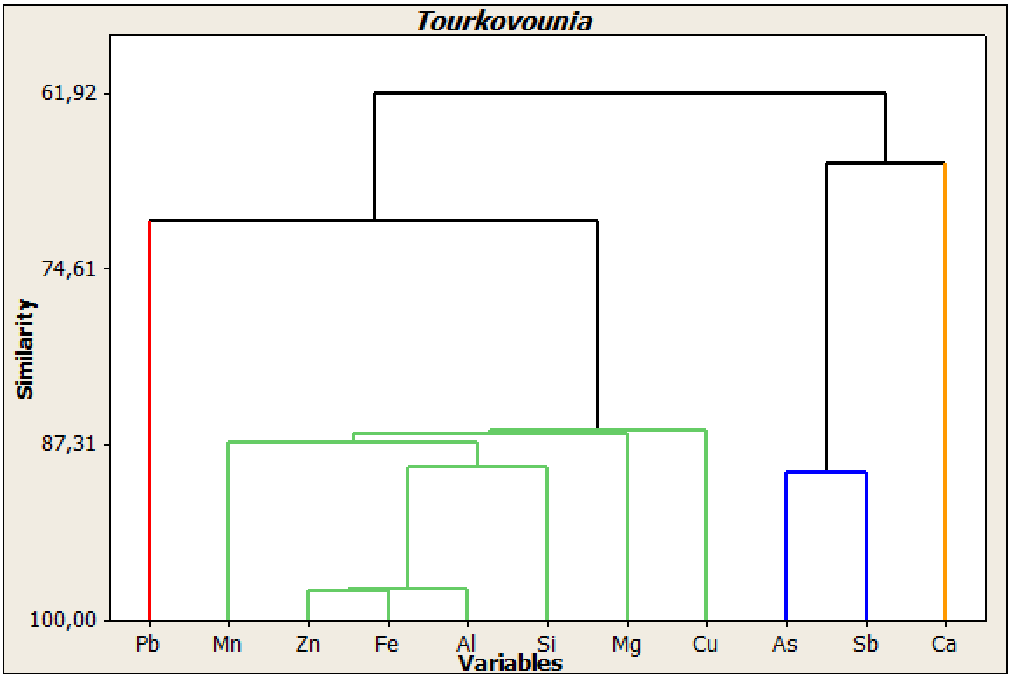

Figure 4.11: Dendrogram for major and trace elements from the Tourkovounia region

-Aigaleo

The samples collected from Aigaleo Mt. comprise mica-schists, cherts, limestones and serpentinites. As with the other sampling areas the dendrograms for the area indicate the petrology and the subsequent mineralogy of the samples collected, especially in the major elements group. Most samples showed zero to negligible contents of arsenic, lead and other potentially harmful elements. Zinc was the only trace element that showed relatively high amounts. On the other hand, chromium recorded the highest concentrations among all other PHEs. Nevertheless such amounts can be attributed to the presence of serpentinites in the sampling area.

In the major elements group the relations among the elements depict the various lithologies comprising the area. Manganese, chromium, iron and nickel form a distinct group that pinpoint the serpentinites rocks found in the area. Calcium's correlation with the former elements can ascribed to the intercalation of the limestones with the serpentinite bodies. The alkalis along with silica form a separate group that shows the argillaceous schists outcropping in the area. Magnesium forms a group of its own because of the presence of magnesite veins inside the serpentinites (Figure 4.12).

As for the trace elements groups, the relations among the elements pinpoint again the various lithologies met in the area. Even where the concentrations of specific elements are negligible e.g. arsenic, lead etc. they have been used to construct the dendrograms as they may provide some useful indications (Figure 4.13). The first group in the trace elements comprises zinc, chromium and nickel. Again this group depicts the presence of ultramafic bodies. The former group is correlated with copper and vanadium that can be found both in the serpentinite bodies and the iron-ores found in the area. Sulfur shows a relation with most of the aforementioned elements but especially with copper and vanadium. This relation indicates the iron-ores where chalcopyrite crystals have been observed during the mineralogical analysis. Lead and arsenic form a group of their own that shows a relation with all the aforementioned groups but especially with sulfur. This relation can be attributed to presence of iron-ore formation in the area.

A combined dendrogram that depicts the relations between major and trace elements has also been constructed (Figure 4.14), because of the small concentrations of some elements and the variety in the lithologies sampled from the area. In this diagram we see that zinc chromium and nickel form a distinct group with manganese and iron verifying in that way their relation with the serpentinite bodies. Potassium, alumina and copper form a group that is related with the former group and both these with calcium. This relation can be explained in terms of the intercalation of the serpentinite bodies with the limestones and the iro-ores. Silica and magnesium form a separate group that is combined with all the aforementioned. In geological terms this relation indicates the mélange-type formation between Al-schists, serpentinites, Fe-ores and limestones that dominates in the region.

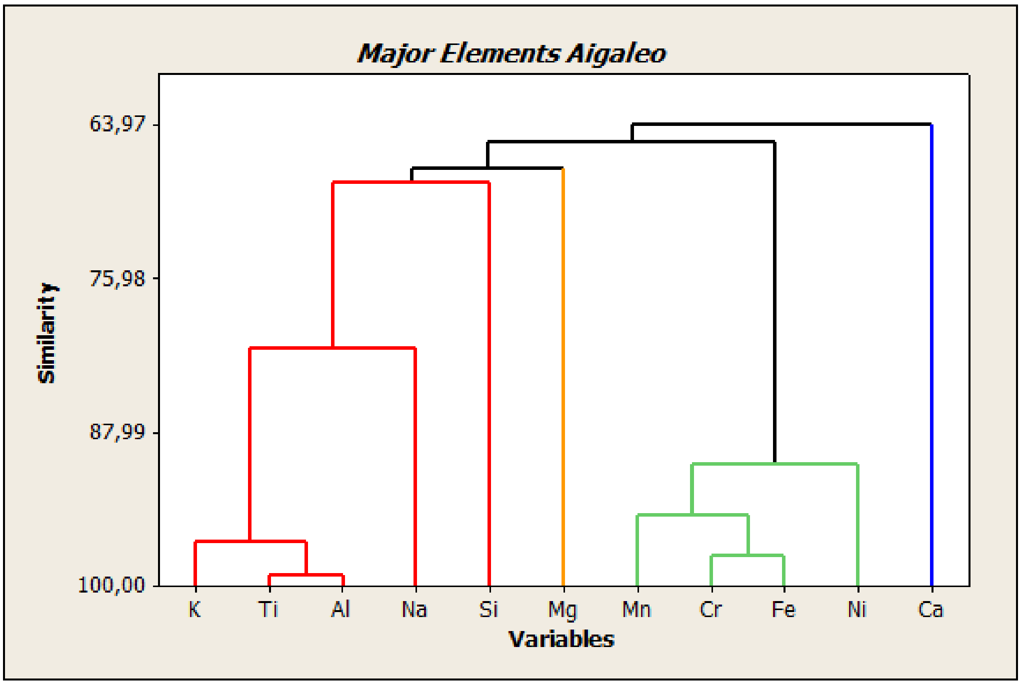

Figure 4.12: Dendrogram showing the major elements in the sampling region of Aigaleo

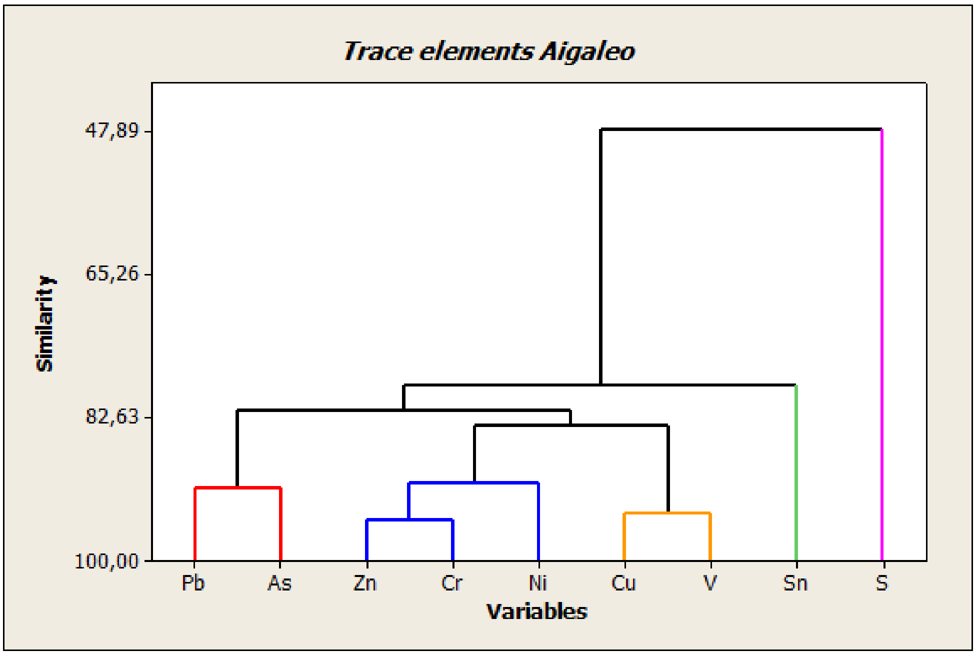

Figure 4.13: Dendrogram depicting the trace elements relation in Aigaleo sampling area

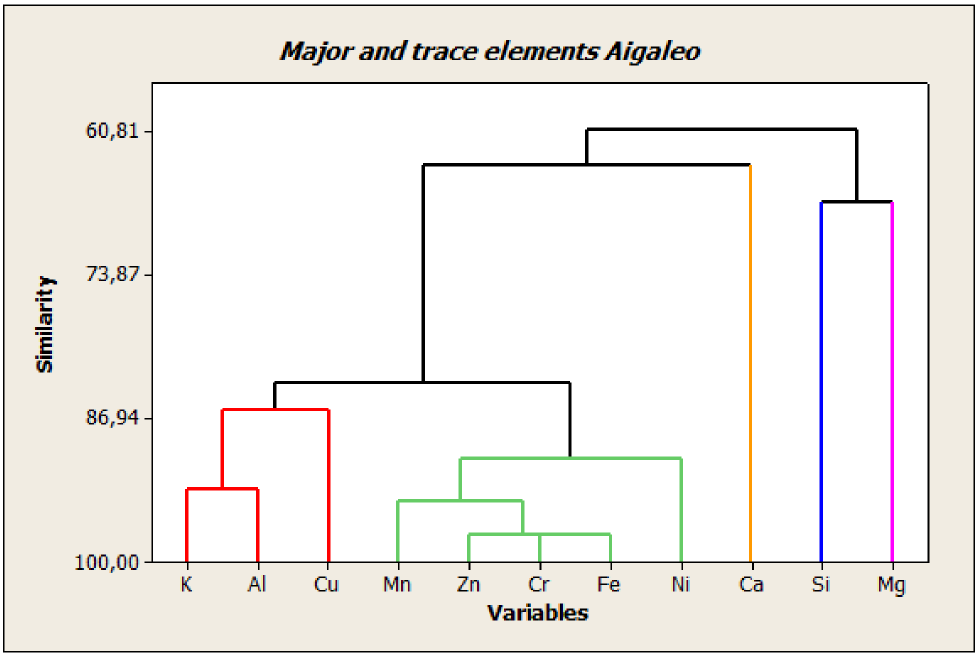

Figure 4.14: Dendrogram showing the relations between major and trace elements in Aigaleo area

4.3 Arsenic associations with lithology

The combined results from each chapter depict some serious evidence about the provenance of arsenic and other potentially harmful elements.

Based on the analyses the highest concentrations of arsenic are located in the central and western parts of the basin of Athens. The areas that recorded the highest average concentrations are Tourkovounia in the north-central part of the basin and the flanks of Hymettus Mt in the western part of the basin. In these areas high As is found mainly inside specific rock types. The highest concentrations are inside the paleosole formations which reach up to 320 mg/kg (sample StT5) and in the metamorphosed mica-schists that were highly affected by weathering phenomena (up to 100 mg/kg). In terms of Unit classification, the Athens Unit hosts the largest amounts of arsenic with the Basement Unit following. The lowest concentrations of the element come from the Sub-Pelagonian Unit.

In each sampling area, distinct lithologies are met. As a result, based on the rock-type met in each region, arsenic shows specific relations with different elements. In Hymettus area As shows a specific preference towards copper and lead. This relation does not indicate chemical affinity rather the simultaneous presence of the elements in the samples and the same behavior when the quantity of one was increasing or decreasing. This relation can be explained by the presence of small (arseno)-pyrite crystals observed inside the mica-schists and the quartz-veins intercalating these formations. In Tourkovounia area arsenic shows a specific preference towards antimony. In Aigaleo area Ni. Cr, Mn, Zn anf Fe show a very good correlation with each other. The relation can be explained by the outcropping of ultramafic bodies in the broader region.

To sum up the statistical analysis mirrors the spatial and chemical affinity of various PHEs in the lithologies met in Athens Basin.

CHAPTER 5: INDEX OF GEOACCUMULATION AND ENRICHMENT FACTOR

5.1 Calculation of Igeo and EF

In order to examine the possible contribution of the various lithologies outcropping in the Basin of Athens to the soil geochemistry of the area, the Index of Geoaccumulation (Igeo) and the Enrichment Factor (EF) have been used. Soil-sample values used for the present estimations come from Argyraki and Kelepertzis (2014).

Igeo has been used as a measure of bottom sediment contamination since the 1970s (Müller, 1979). It determines contamination by comparing current metal contents with pre-industrial levels (Müller, 1981). The content accepted as background is multiplied each time by the constant 1.5 in order to take into account natural fluctuations of a given substance in the environment as well as very small anthropogenic influences. The value of the geoaccumulation index is described by the following equation:

$$\boldsymbol{I}_{geo} = \mathbf{log_2} \frac{\boldsymbol{C}_{\mathrm{n}}}{1.5 \times \mathrm{B}_{\mathrm{n}}}$$

where:

Cn - element content in tested soil (here concnetrations from Argyraki and Kelepertzis, 2014),

Bn - background content; here the average element content in the samples from each region.

The interpretation of the obtained results is as follows:

$Igeo \leq 0$ practically uncontaminated,
$0 < Igeo < 1$ uncontaminated to moderately contaminated,
$1 < Igeo < 2$ moderately contaminated,
$2 < Igeo < 3$ moderately to heavily contaminated,
$3 < Igeo < 4$ heavily contaminated,
$4 < Igeo < 5$ heavily to very heavily contaminated and
$Igeo \geq 5$ very heavily contaminated.

The use of the enrichment factor (EF) is for the assessment of the anthropogenic contamination in the study area (Loska et. al, 2002). Its version adapted to assess the contamination of various environmental media is as follows:

$$EF = {\frac{C_n}{C_{ref}}} \Big/ {\frac{B_n}{B_{ref}}}$$

where:
C_n - content of the examined element in the examined environment,
C_{ref} - content of the examined element in the reference environment,
B_n - content of the reference element in the examined environment,
B_{ref} - content of the reference element in the reference environment.

An element is regarded as a reference element if it is not correlated with human activities. Such elements are Al, Fe, Li, Ga, Sc and rare earth elements. Aluminum has been used as a reference element. Again the average values of each element from each region have been as background values. Five contamination categories are recognized on the basis of the enrichment factor:

EF < 2 – depletion to minimal enrichment,
EF = 2-5 – moderate enrichment,
EF = 5-20 – significant enrichment,
EF = 20-40 – very high enrichment,
EF > 40 – extremely high enrichment (Sutherland, 2000)

Despite certain shortcomings (Reimann and Karitat, 2000), the enrichment factor, due to its universal formula, is a relatively simple and easy tool for assessing enrichment degree and comparing the contamination of different environmental media.

The average content for each element for each sampling area from the present research have been used as geochemical background values. The soil values from the research by Argyraki and Kelepertzis (2014) have been used to determine the EF and Igeo numbers. The samples chosen can be found in the Appendix C (Tables 1 and 2). Care was taken the sample-values picked from the aforementioned research to be located in a very close proximity with the rock samples collected during the present research. Moreover the values for each element for the Upper Continental Crust have been used in order to examine the possible enrichment of specific elements in the samples from each region.

Before the estimation of EF and Igeo another assessment has been made. In the diagram that follows (Figure 5.1) the average values for a set of elements has been divided with the content of these elements in the Upper Continental Crust. The classification was based on the area of sampling. The assumption that was made was that the chemistry of the rocks sampled represents the average geochemistry of the whole area.

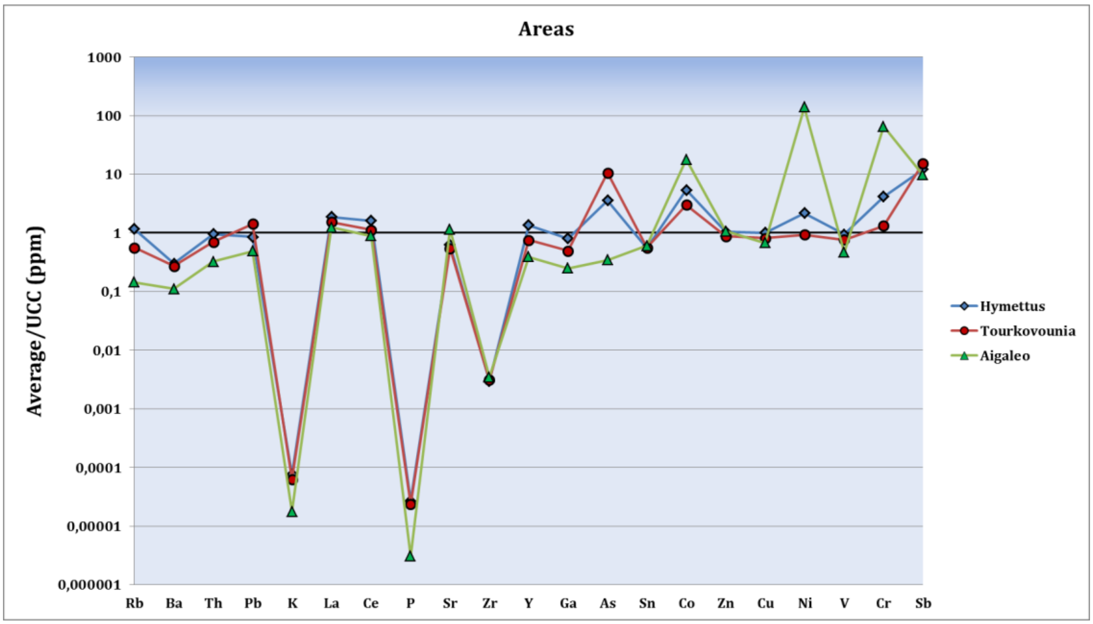

Figure 5.1: Average values for trace elements in the sampled areas divided by the values of the UCC.

What we see from this diagram is that in the areas of Hymettus and Tourkovounia arsenic shows an enrichment of up to 10 times (4.8ppm for the UCC). Lead shows a small enrichment in Hymettus area whereas antimony shows a significant enrichment in all the regions (0.4ppm for the UCC). Nickel and chromium depict enrichment in the area of Aigaleo. This can be the outcome of the presence of ultramafic rocks.

Apart from these elements most of the others show minor enrichment or depletion with regard to the values found in the UCC. Only potassium, zircon and phosphorus record a major depletion. Regarding phosphorus this major depletion can be attributed in biases during the analytical procedure.

The importance of this diagram is that it defines in a quantitative manner the geochemical baseline values of the study areas. These values are important because they were used in order to estimate the Igeo and the EF for the all the areas. This practically means that in the cases where elements record a significant enrichment or depletion the values of Igeo and EF will be higher or lower in respect in comparison to the actual values. However the quantitative conclusion of this diagram is that the enrichment of some elements is correlated with geogenic sources.

-Hymettus

For the same set of elements the geoacummulation index for Hymettus area shows a clear enrichment in all of them (Figure 5.2). The usage of the term contamination cannot be applied for specific elements e.g. rubidium, strontium etc. Moreover as the baseline values are already enriched the geoacummulation index is expected to show greater results for some elements e.g. nickel or rubidium. Nevertheless, arsenic, lead and chromium show a significant enrichment. As is almost 8 times more compared to the average values for the area, Pb values are 7 to 12 times higher and Cr values 13 to 15 times higher. According to the proposed nomenclature the soils in the area of Hymettus can be classified as contaminated. Keeping in mind the fact that the baseline values for these elements are already high, the extent of contamination for the soils in high but not so high indicated by the diagram.

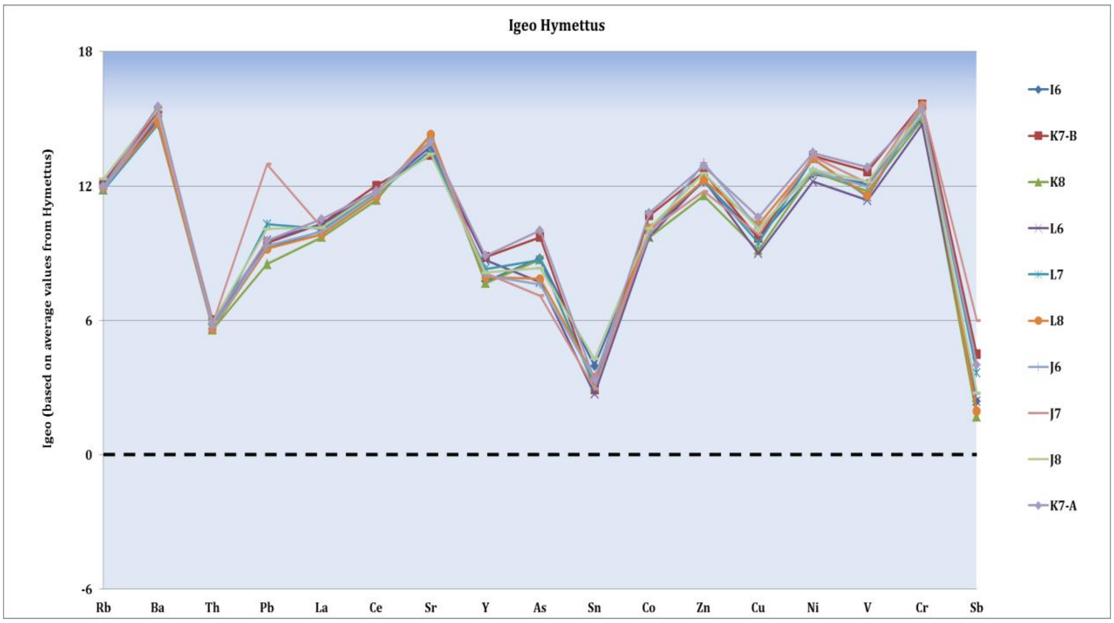

Figure 5.2: Diagram showing the Igeo for soil-samples from the Hymettus area

The EF for the same set of samples and elements (Figure 5.3) shows depletion from anthropogenic factors for the elements arsenic, tin, copper, antimony and lead and enrichment for barium and chromium. More precisely As records values of 1 to ~ 0.2 with these values indicating the small contribution of anthropogenic factors to the content of the elements in the soil and so its natural derivation. Zinc and nickel show that their origin can be attributed to both anthropogenic and natural factors as their values range from ~ 3 to 0.8. Also the derivation of Pb indicates both natural and human factors with values ranging from 10 to 0.6. Bearing in mind that the values for some elements are already enriched as the baseline values are high then the EF for some elements must be even lower. This enhances even more the argument of the natural derivation of some elements such as arsenic.

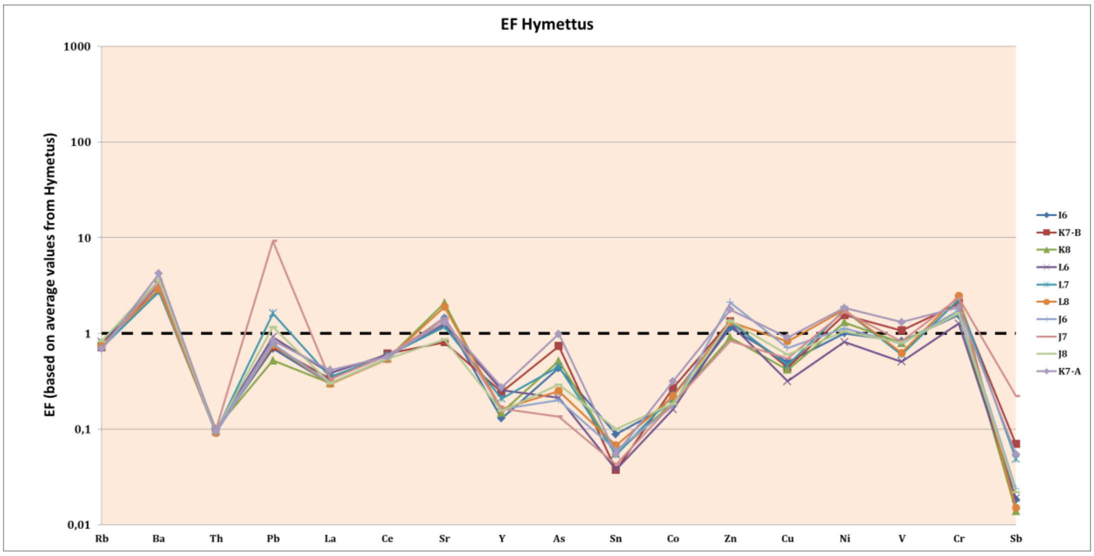

Figure 5.3: EF diagrams for the samples from Hymettos area

- Tourkovounia

For the area of Tourkovounia the values of Igeo for all the samples show a significant enrichment with regard to the average values for the area (Figure 5.4). Only tin shows a lesser enrichment in comparison to the other elements. More accurately, As is ~ 8 to 13 times higher, Zn ~ 10 to 13 times more, Pb ~8 to 11 orders higher and Cr ~ 12.5 to 14 times higher. Also the elements Rb, Ba, Th, La, Co and Ni record significant values of enrichment from ~ 4 to 16 times. Sb records enrichment in the order of ~ 2 to 4 times. As a result the soil-samples from this region can be classified as highly contaminated in specific elements such as arsenic, zinc, lead, copper and antimony. Again we must keep in mind the fact that the baseline values for some elements are high. As a result the extent of contamination for the soils will be high but not as high as indicated by the diagram. In this area though only As shows great values but again the contamination in the soils is classified as heavy.

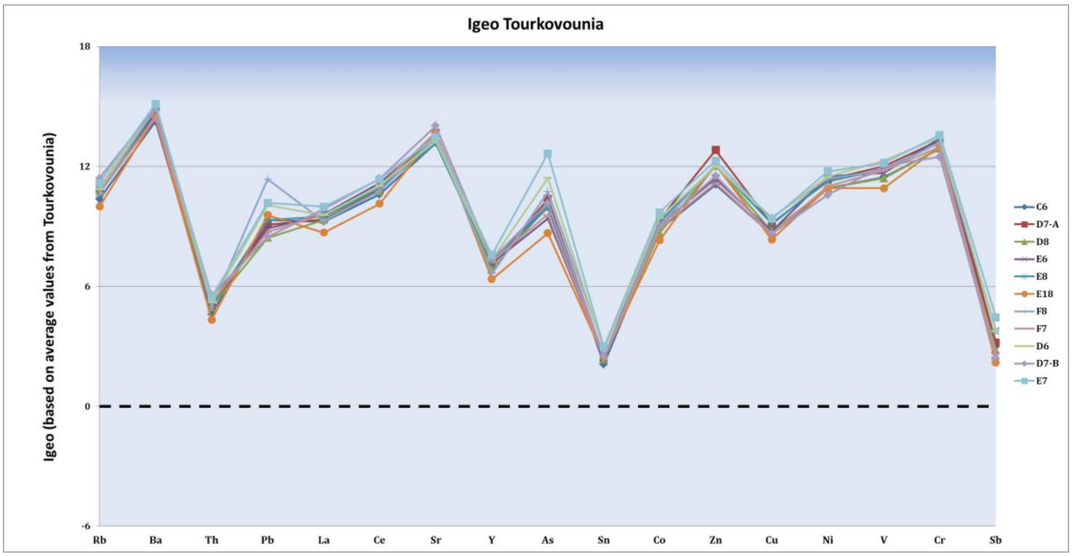

Figure 5.4: The Igeo values for the samples from Tourkovounia area

The values of EF for Tourkovounia area show low values for arsenic, tin and antimony. On the other hand zinc records high values. More precisely Pb records both high and low values ranging from ~ 0.2 to 8 (Figure 5.5). Thus its enrichment can be attributed to both natural and anthropogenic factors. The same conclusions can be drawn from the values nickel. The values of As, Sb and Sn show that their derivation is primarily natural as they range from ~ 0.03 to 0.9. On the other hand Zn shows a clear human derivation with values ranging from ~ 0.9 to 8. These results indicate the geogenic origin of the elements arsenic, tin and antimony and the anthropogenic origin of zinc. The values for lead indicate that both natural and human factors contributed to the dispersion of the element in the soil.

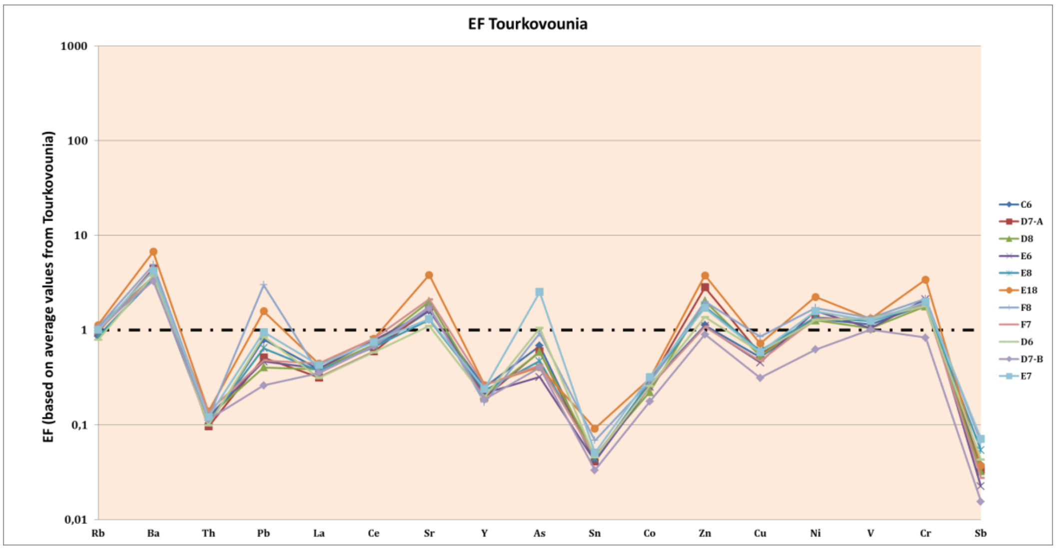

Figure 5.5: EF values for soil samples from Tourkovounia area

- Aigaleo

The geoacummulation index for Aigaleo region shows high values for nickel, chromium and zinc (Figure 5.6). More specifically Ni and Cr record the highest values ranging from ~ 19 to 24. As, Pb and Zn show significant values of contamination with values from ~ 6 to 12. Thus the soil around the area of Aigaleo can be classified as contaminated in these elements. What is needed to be deciphered is the provenance of these elements in the soil samples.

The application of the EF for the samples revealed that As, Pb and Sn have very low values ranging from ~ 0.2 to 1 (Figure 5.7). As a result no enrichment due can assumed for these elements in the soils. Moreover as their concentrations to the rock samples are very small i.e ~ 1ppm, 8ppm and 3ppm, respectively, one can assume that every content of these elements found in the soil can be only attributed to human activities. The small though positive values of EF for Ni, Cr i.e. ~2 to 3 verify their natural origin in the soil. The later conclusion can also be testified by the outcropping of serpentinite bodies cropping in the broader area.

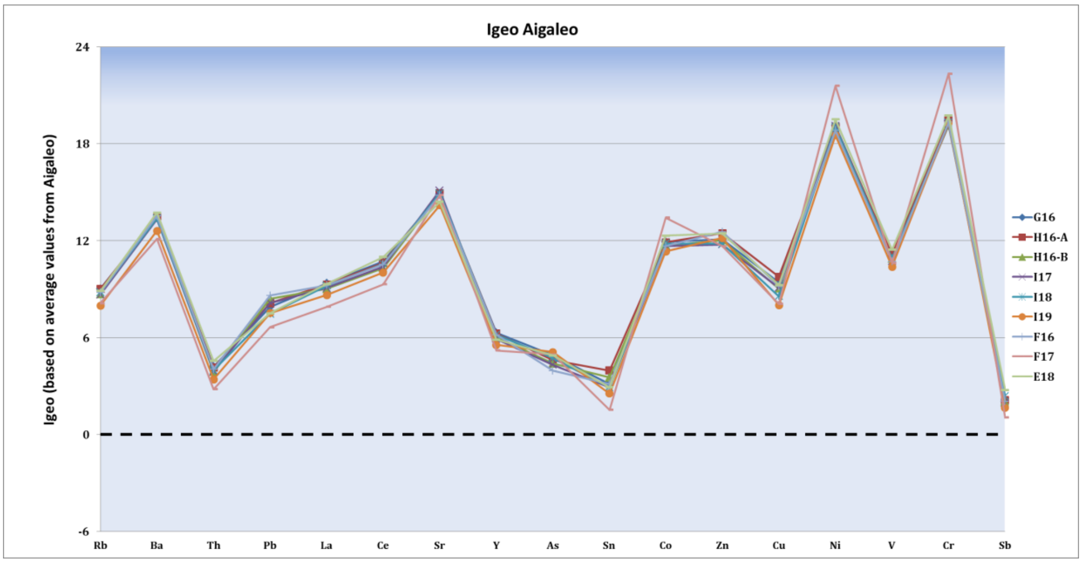

Figure 5.6: Igeo diagram for the samples from Aigaleo area

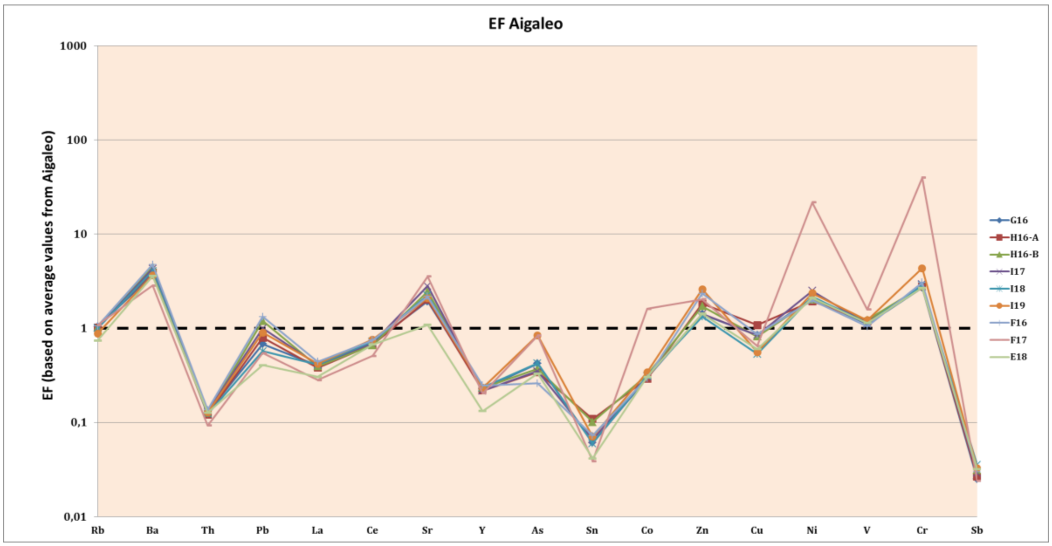

Figure 5.7: EF values and diagram for the samples from Aigaleo area

5.2 Discussion of elemental origin in the Athens Basin

Based on the results one can assume that for most elements there is a fraction that its origin can be attributed to natural/geogenic factors. That fraction changes from element to element and from area to area. For example As in the area of Tourkovounia seems to have a natural provenance in the soil whereas in Hymettus seems to have both anthropogenic and natural origin. In order to examine the validity of the results of the present research, a comparison was made with recent works conducted in the region. These researches include the one from Kelepertzis et al. (2016), and from Kampouroglou and Economou (2016).

Kelepertzis et al. (2016) examined the isotopic signature of Pb from a variety of samples from the Basin of Athens. The samples ranged from rock-samples to home-dust samples and soil samples. The samples examined have a spatial connection with samples from Hymettus area from the present research. The isotopic analysis showed that the origin of Pb in the soil samples can be apportioned to two different sources, the two end members, geogenic and anthropogenic in nature suggesting a simple mixing model (Ettler et al., 2004; Komárek et al., 2008). The natural contribution to soil Pb is represented by the isotopic ratios of the bedrock samples. The Pb isotopic ratios of the collected parent materials define a single ^{206}Pb/^{207}Pb ratio that is representative of the lithogenic background (^{206}Pb/^{207}Pb = 1.200). Moreover the percentage contribution of human activities, in this case, vehicular emissions, to the total Pb found in the soil of Athens, ranged from 36% to 95% depending on the area of interest. The results from the present research indicate the same thing for the provenance of Pb in the Hymettus. That its origin is attributed to natural or anthropogenic factors with the latter being the most likely. The natural factors comprise the derivation from the lithologies and the various pedogenic reactions that can lead into enrichment inside the soil.

Kampouroglou and Economou (2016) examined the concentrations of As and heavy metals in lacustrine travertine limestones and soils from the broader region of Athens. The travertine limestones showed significant contamination in As and other heavy metals. Other major sources of contamination that have been identified are the sulfide and Fe-Mn ore deposits located in the NE tips of Athens, the basement rocks and the ophiolite blocks cropping out around Athens. The samples from Kampouroglou and Economou (2016) that overlap with the present research come from Hymettus area. Unfortunately, no published mapping data exist on the specific location of the travertine limestones and there was no evidence of their existence during the survey of the present study. Despite the fact that no travertine limestones have been sampled during the present research the conclusion that arsenic and other heavy metals seem to have a natural origin is a commonplace in both studies. Some metal(oid)s has been proved to have a binary or an anthropogenic origin e.g.. Pb and Zn (Argyraki and Kelepertzis, 2014; Kelepertzis and Argyraki, 2015; Kelepertzis et al., 2016). Nevertheless As, Ni and Cr seem to come predominantly from the bedrock and their dispersion and subsequent enrichment in the soil of Athens can be attributed to weathering processes. Deciphering the origin of all these elements is of prime importance in order to assess any possible impact to human health. This assessment will determine the environmental policy and countermeasures public services should follow.

CHAPTER 6: CONCLUSIONS AND FURTHER RESEARCH

6.1 Conclusions

Rock samples from Hymettus, Tourkovounia and Aigaleo areas, in the west, northwest and east of the Basin of Athens respectively, have been collected and analysed within the frame of a lithogeochemical study of near surface bedrock in the Athens Basin. From the results of the research we see that the relations and the origin of both major and trace elements changes in various ways. More precisely:

The statistical analysis revealed that major- elements relations demonstrate the various lithologies occurring in the Basin of Athens.

Arsenic shows relative enrichment in the various carbonate lithologies that span around Athens and especially in paleosol- type material found within them.

In terms of geological unit classification the carbonate rocks of Athens Unit, occurring in Tourkovounia contains the highest average values of PHEs i.e., As (50 mg/kg), Zn (58 mg/kg) and Pb (24 mg/kg).

The average values for each element from all the samples collected from each distinct region has been used as geochemical baseline values. The results divided by the values of each element for the Upper Continental Crust revealed that there is siginificant enrichment in certain trace elements such as arsenic, cobalt, nickel and chromium. On the other hand some trace elements showed neither enrichment nor depletion whereas some showed major depletion. The elements that showed major depletion are P and Zr. The elements that showed neither condition are Pb, Sn, Zn, Cu and V. These results indicate that rock samples, occurring in the study area are enriched in some elements and have the potential to contribute to high concentrations of PHEs in urban soil.

The Igeo for soil samples collected in the study areas by Argyraki and Kelepertzis (2014) reveals that the soil from the areas of Hymettus and Tourkovounia is highly impaired from elements such as arsenic, lead, chromium and zinc. Aigaleo area is impaired predominantly by chromium and nickel.

The EF values indicate the contribution of human activities in the soil. Based on the results what we see is that some elements seem to have a binary origin whereas others seem to have only natural or only anthropogenic. Arsenic in Tourkovounia seems to come from the various lithologies comprising the area, while in Hymettus and Aigaleo may be derived from both natural and human factors. Zinc seems to come from human sources in all the above mentioned areas.

6.2 Further Research

Although the present study provided further evidence on the geogenic origin of some significant PHEs in the Athens environment some suggestions for further research are made.

Firstly the examined rock database can be expanded to include additional rock types of the Athens Basis such as post alpine rocks that were not examined at this stage. Furthermore the Lavrion area, located 35km in straight line from the center of Athens, hosts a number of ore-deposits with very high PHEs and especially arsenic contents. Weathering phenomena along with supergene reactions can lead into the enrichment of arsenic in the soils. Also, the structural framework of Athens would allow the transferring of hydrothermal fluids, during the creation of the deposits, which would lead to an enrichment of the country rock.

In addition to both cases, the transferring of arsenic through the aquifers must be taken into account, as the interaction of groundwater with As-bearing rocks has been proposed as one of the possible sources of arsenic enrichment in groundwater and soils (Armienta et al., 2000).

Rock samples from the deeper, unweathered environment should also be considered for analysis, as it is possible that weathering phenomena expert a great influence on the rock outcrops examined in the present study. An opportunity to gather such data exists by considering samples from the drilling core archive of the Athens Metro. The examination of the transition from the weathered environment to the primary, unweathered rock may provide useful information on the evolution of elemental mobilisation processes.

Finally, a more detailed mineralogical analysis of rock samples is also suggested in order to find possible mineral-carriers of As and other PHEs in the primary geologic environment compare them to their weathering products in the surface media such as soil. This should include optical microscopy as well as SEM-EDS analysis.

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APPENDIX A – SAMPLE DETAILS

Sample id	Latitude	Longitude	Rock Type
StK1	37°57'66.7"N	023°46'21.2"E	marble
StK2	37°57'66.7"N	023°46'27.7"E	marble
StK3	37°57'91.5"N	023°47'00.8"E	dolomite
StK4	37°57'47.9"N	023°47'07.6"E	mica-schist with qtz vein
StK5	37°57'47.9"N	023°47'07.6"E	quartz vein
StK6	37°57'47.9"N	023°47'07.6"E	mica-schist highly oxidized
StK7	37°57'49.5"N	023°47'24.8"E	mica-schist highly oxidized
StK8	37°57'48.2"N	023°47'33.5"E	mica-schist
StK9a	37°57'46.7"N	023°47'40.2"E	mica-schist
StK9b	37°57'46.7"N	023°47'40.2"E	qtz vein
StK10	37°57'45.8"N	023°47'47.6"E	mica-schist
StK11	37°57'45.8"N	023°47'47.6"E	mica-schist (very altered)
StK12	37°57'45.8"N	023°47'47.6"E	mica-schist
StT1	38°01'07.4"N	023°45'79.1"E	limestone
StT2	38°01'02.7"N	023°45'84.2"E	oxidized limestone
StT3	38°01'02.7"N	023°45'84.2"E	paleosole
StT4	38°01'02.7"N	023°45'84.2"E	limestone
StT5	38°01'02.7"N	023°45'84.2"E	paleosole
StT6	38°01'03.4"N	023°45'88.1"E	oxidized formation inside the limestones
StT7	38°00'46.7"N	023°45'68.1"E	quartz vein
StT8	38°00'46.7"N	023°45'68.1"E	volcanic
StT9	38°00'46.7"N	023°45'68.1"E	volcanic - volcanoclastic
StT10	38°00'46.7"N	023°45'68.1"E	clasts from inside the volcanic formation
StT11			marble from Filothei
R1	37°59'44.1"N	023°39'34.7"E	qtz-schist
R2	37°59'44.1"N	023°39'34.7"E	schist
R3	37°59'44.1"N	023°39'34.7"E	Al-schist
R4	38°00'06.7"N	023°39'10.1"E	Al-schist
R5	38°00'03.2"N	023°39'10.8"E	pelagic limestone
R7	37°59'59.4"N	023°39'08.7"E	Fe-ore
R8	37°59'59.4"N	023°39'08.7"E	serpentinite with magnesite
R11	37°59'55.9"N	023°39'03.5"E	Cretaceous limestone
R15	37°59'90.3"N	023°38'97.4"E	siliceous-magnesite
R16	37°59'90.3"N	023°38'97.4"E	serpentinite
R19	37°59'90.7"N	023°38'99.4"E	chert
R21	38°00'01.0"N	023°39'15.3"E	serpentinite
R26	37°59'98.9"N	023°39'11.3"E	Fe-ore inside serpentinite
ΜΕΤΣ			limestone with ankerite
LYK			limestone
EKA			marble
ΕΚΑΛΗ			paleosol (From joints in marble)

ILI	schist
ΖΩΓΡΑΦΟΥ	schist
ΚΥΡ	volcanic (metabasite)

CRM	**Rock Type**
JLs-1	limestone
JGb-1	gabbro-1
JR-2	rhyolite
JB-3	basalt
JG-3	gabbro-3
JA-3	andesite
JF-2	feldspar

APPENDIX B – XRD DIAGRAMS

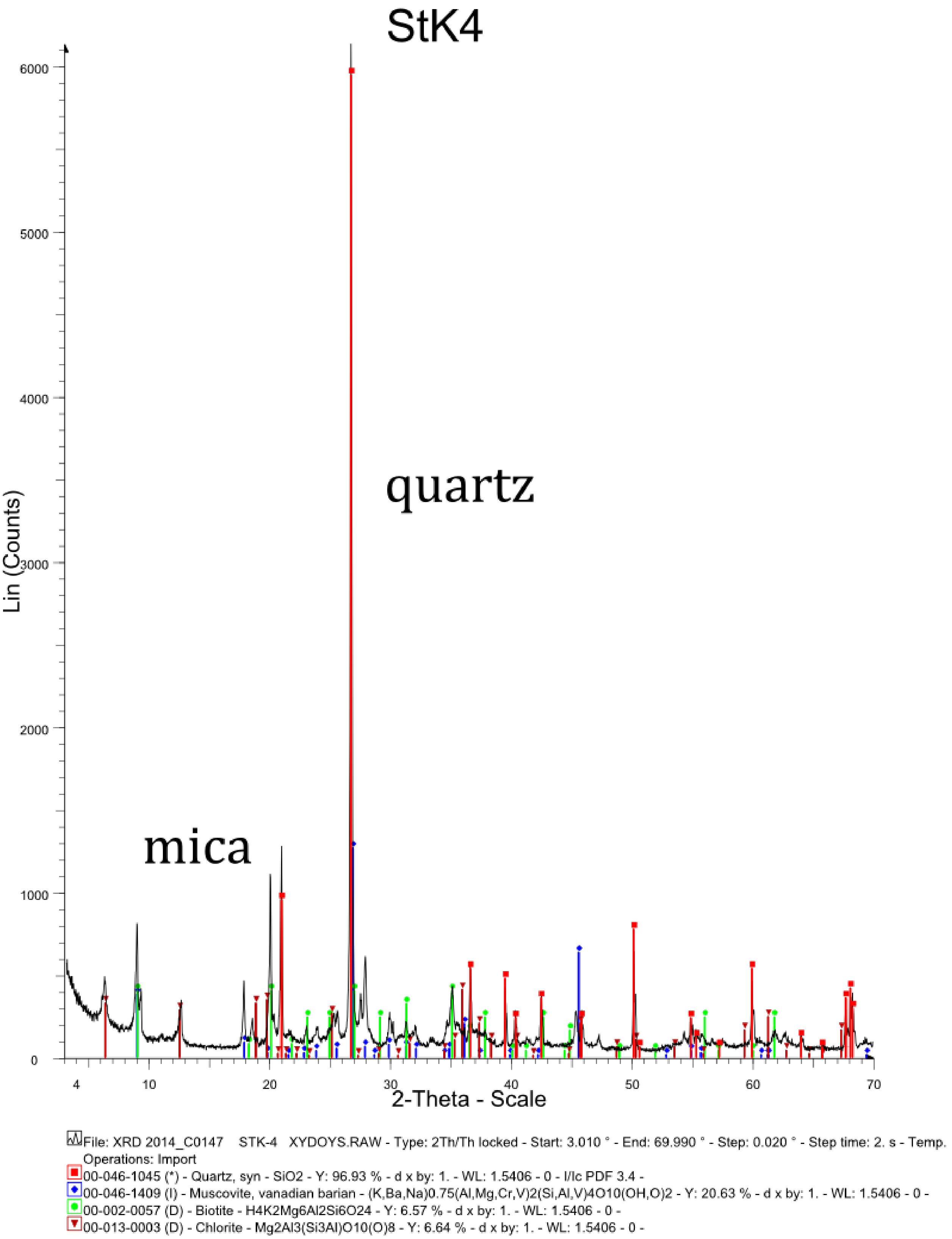

Figure 1B: XRD diagram of sample StK4

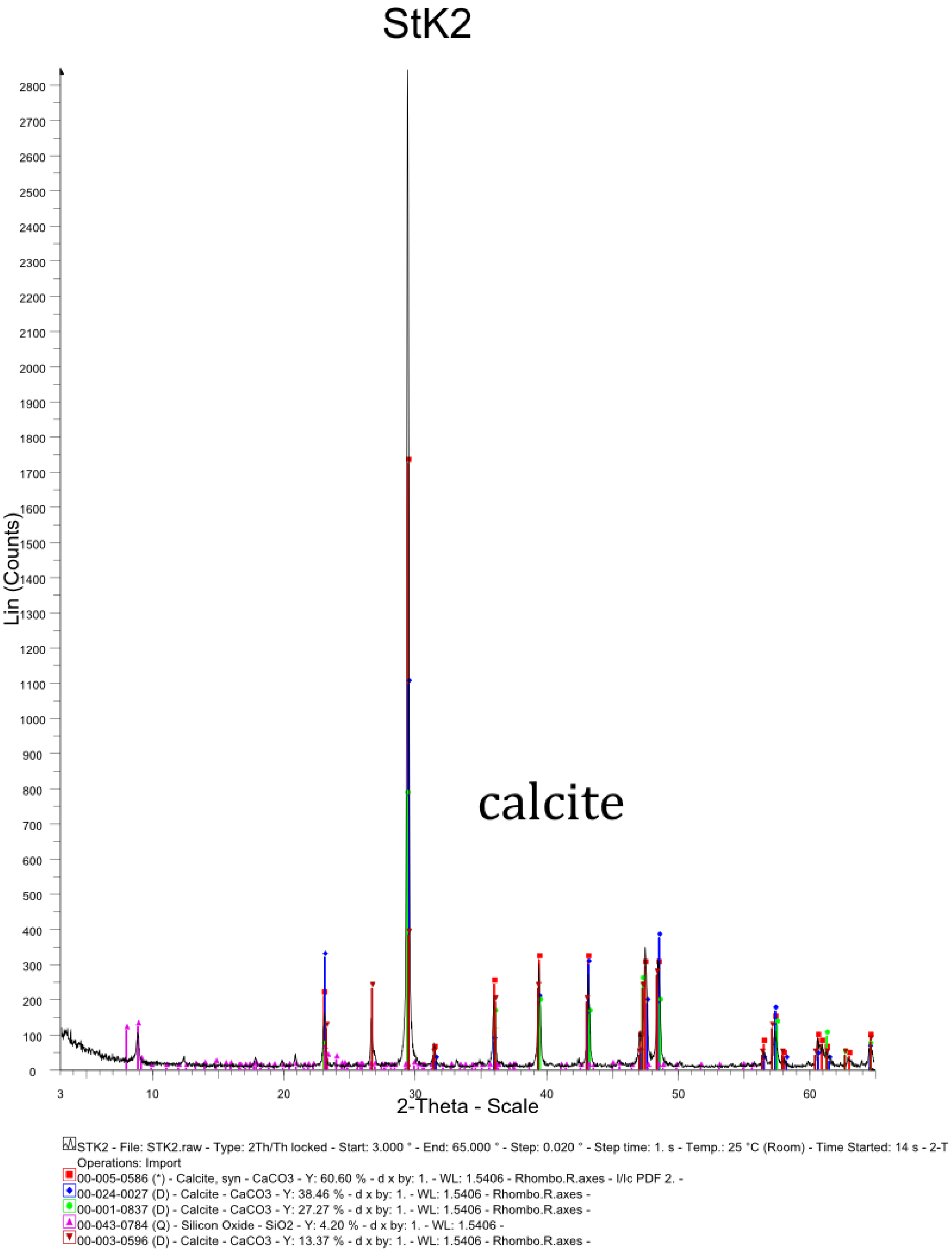

Figure 2B: XRD diagram of sample StK2

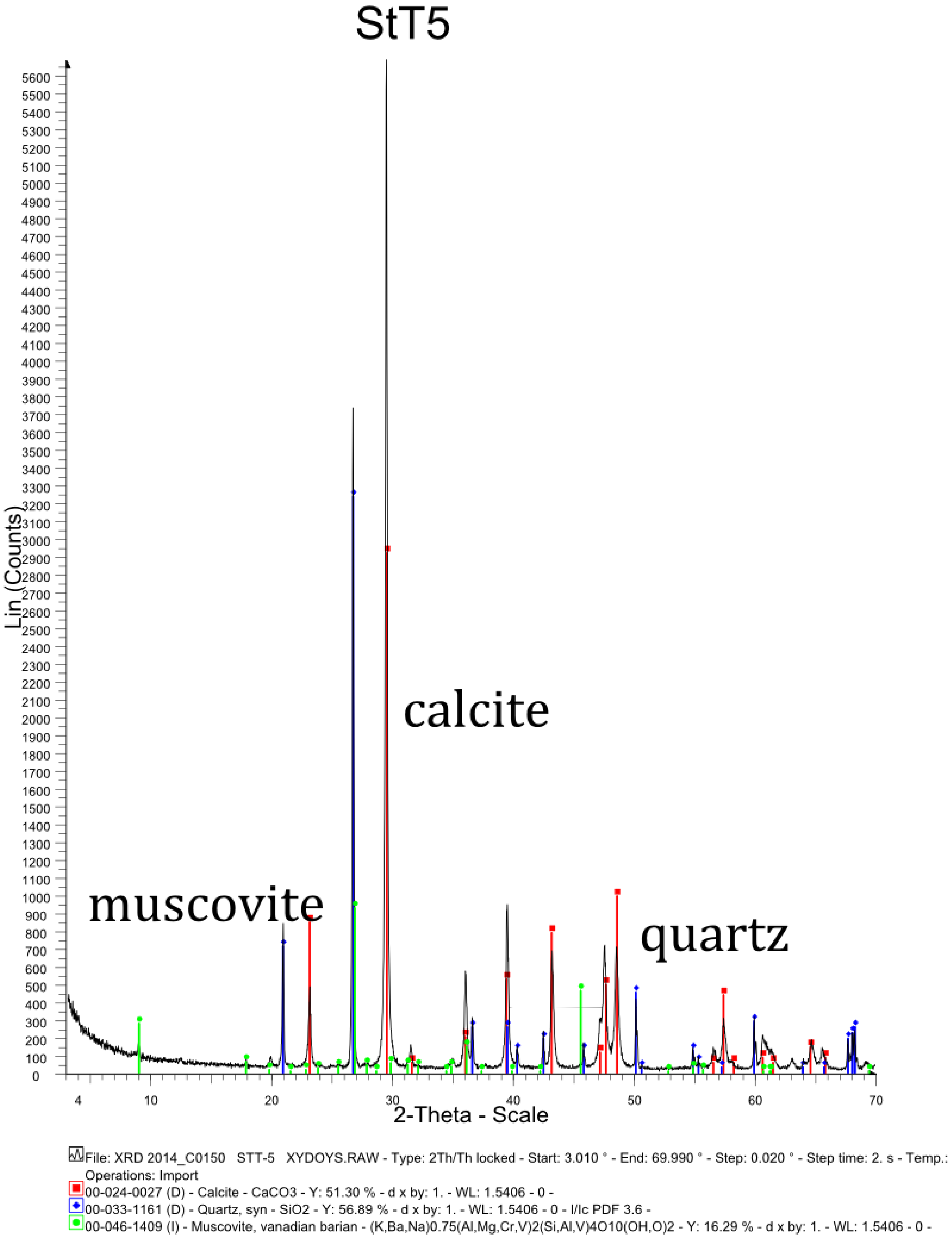

Figure 3B: XRD diagram of sample StT5

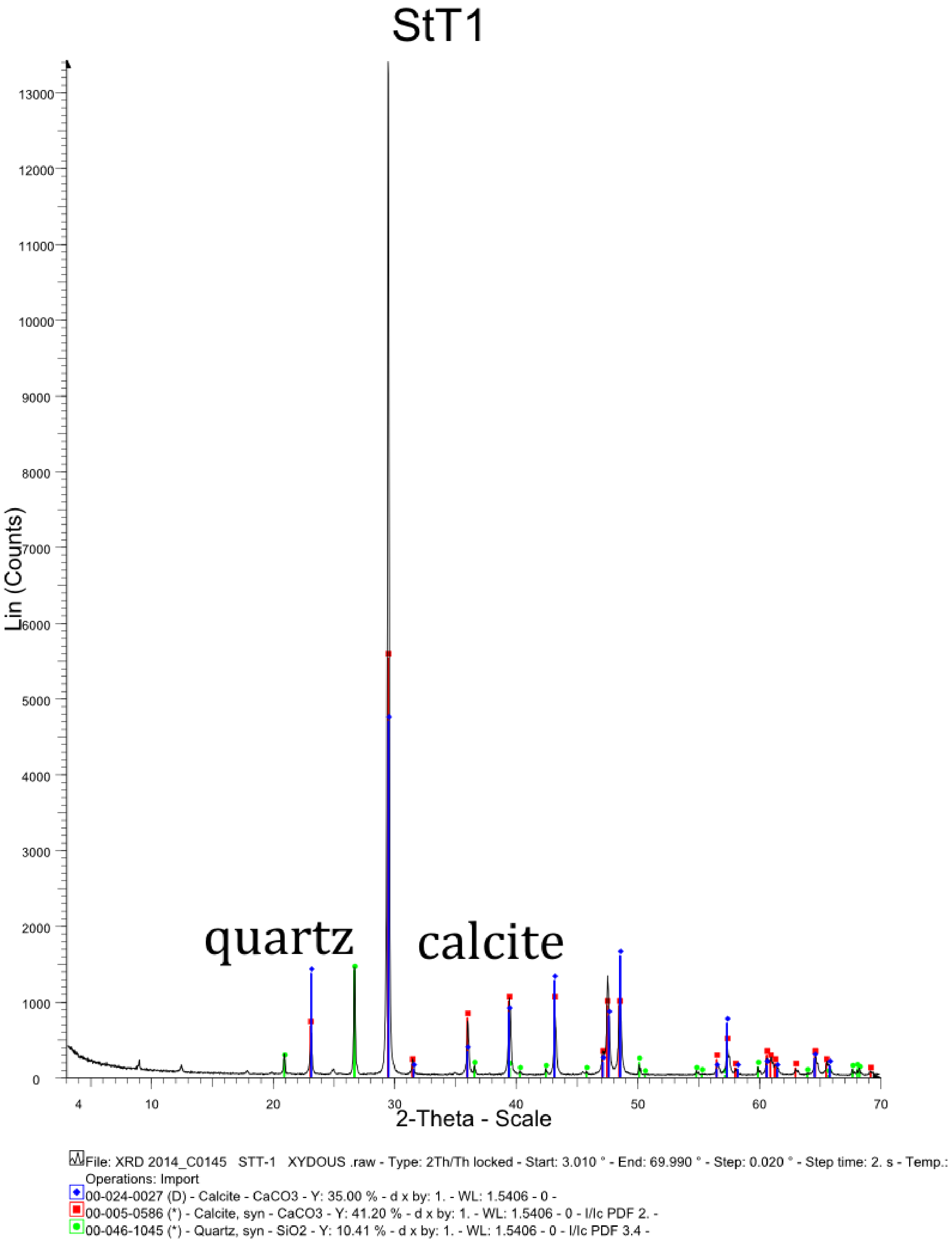

Figure 4B: XRD diagram of sample StT1

APPENDIX C – CORRELATION MATRIX

Correlation Matrices

Following the statistical analysis, correlation matrices have been created for all the samples combined and for each sampling area separately. The goal was to verify the relations between the various elements showed by the various boxplots and dendrograms.

Initially a correlation matrix has been created for all the samples (Table 1B). The strong correlation between major elements is verified. This fact shows the various lithologies sampled. Moreover this matrix pinpoints the good correlation for arsenic and antimony (~ 0.6). All these data verify the boxplots and dendrograms created for the whole package of the analyses. Correlation matrices for each distinct sampling area have been created. In each case the relations between the elements have been examined.

For the Hymettus area, boxplots and dendrograms revealed relations between the pairs manganese-arsenic and zinc-copper. The correlation matrix showed that both pairs have a very good relation (~0.72) (Table 2B).

For Tourkovounia area the statistical analysis correlated the following elements: arsenic with antimony, zinc with copper, manganese, iron, nickel and alumina. Indeed the correlation matrix revealed a very good correlation of arsenic with antimony (~0.78) and good relations between the other elements ranging from 0.72 to 0.77 (Table 3B).

For Aigaleo area the pairs that have been showed to have a relation during the statistical analysis are zinc with copper, zinc with manganese, zinc with nickel and copper with potassium and alumina. The values for the first three pairs are 0.67 0.87 and 0.81 in respect. The values for the next two are 0.38 and 0.72 in respect. As a result the relation between copper and potassium must be discarded.

	Rb	*Pb*	*K*	*P*	*Sr*	*Y*	*Ga*	*Ti*	*Mn*	*As*	*Sn*	*Zn*	*Cu*	*Ni*	*V*	*Cr*	*Si*	*Al*	*Fe*	*S*	*Sb*	*Ca*	*Na*	*Mg*
Rb	1																							
Pb	0,16152	1																						
K	0,53285	0,29912	1																					
P	0,06889	0,33613	0,44394	1																				
Sr	-0,1065	-0,1045	-0,1542	-0,1875	1																			
Y	0,242	0,25918	0,65785	0,46245	-0,2296	1																		
Ga	0,39659	0,26748	0,81494	0,42968	-0,2558	0,83513	1																	
Ti	0,46129	0,31347	0,87628	0,48445	-0,2208	0,85254	0,96273	1																
Mn	-0,1599	0,0121	-0,1656	0,05355	0,01849	-0,0492	0,02923	-0,1393	1															
As	-0,043	0,00242	0,01908	-0,1021	-0,0791	-0,0186	-0,0986	-0,0766	-0,0969	1														
Sn	-0,1754	-0,3412	-0,2781	-0,1784	0,21354	-0,1581	-0,0721	-0,1749	0,21623	-0,0118	1													
Zn	-0,0354	0,14515	0,24036	0,16159	-0,3067	0,25044	0,53356	0,34632	0,64885	-0,1305	0,22207	1												
Cu	0,03891	0,10343	0,58012	0,2245	-0,1589	0,43996	0,6052	0,53889	0,38523	0,15839	0,01389	0,65594	1											
Ni	-0,1269	-0,1212	-0,3018	-0,1738	-0,1787	-0,2097	-0,0586	-0,2284	0,63996	-0,1392	0,40917	0,6189	0,06397	1										
V	0,49513	0,37597	0,86805	0,40469	-0,1854	0,76814	0,92044	0,9049	0,09855	-0,0648	-0,1734	0,50577	0,67427	-0,0863	1									
Cr	-0,118	-0,0966	-0,2767	-0,1585	-0,1752	-0,2028	0,02471	-0,1958	0,77836	-0,1284	0,37865	0,71232	0,1752	0,84568	0,00925	1								
Si	0,35836	0,20469	0,44716	0,52316	-0,3683	0,42189	0,45877	0,51977	-0,1271	-0,1594	-0,1856	0,20848	0,06427	-0,053	0,40473	-0,1607	1							
Al	0,42388	0,28532	0,85231	0,45146	-0,2199	0,81776	0,96561	0,98374	-0,1281	-0,0878	-0,1421	0,39104	0,56037	-0,2192	0,88479	-0,1705	0,49479	1						
Fe	-0,0805	-0,0038	-0,1273	-0,0194	-0,2074	-0,0405	0,21145	-0,0044	0,82487	-0,1474	0,28528	0,81795	0,36301	0,73751	0,19571	0,92838	-0,0764	0,02712	1					
S	0,15623	-0,0387	-0,1298	-0,1923	-0,0116	-0,1448	-0,1597	-0,1397	-0,1239	-0,0443	-0,1344	-0,1891	-0,2412	0,00865	-0,0933	0,03172	-0,1216	-0,1555	-0,0651	1				
Sb	-0,0943	0,02683	0,00371	-0,0536	-0,1446	-0,0373	-0,0674	-0,0589	-0,0724	0,59088	-0,0796	0,01206	0,16497	-0,0076	-0,0616	-0,0303	0,06248	-0,0763	-0,0961	-0,0829	1			
Ca	-0,2905	-0,209	-0,447	-0,4744	0,44981	-0,4744	-0,6307	-0,5873	-0,2647	0,21226	0,03409	-0,6171	-0,3209	-0,2831	-0,5682	-0,2757	-0,8206	-0,5879	-0,4097	0,10263	0,04271	1		
Na	0,3054	0,04136	0,38437	0,25851	-0,1326	0,28496	0,51436	0,53939	-0,2129	-0,1671	-0,1078	0,14921	0,13031	-0,203	0,33551	-0,2056	0,47681	0,63041	-0,0587	-0,0659	-0,1292	-0,4534	1	
Mg	-0,1216	-0,1729	-0,2587	-0,1218	-0,095	-0,2069	-0,2252	-0,225	0,03015	-0,1491	0,15366	-0,012	-0,2284	0,22387	-0,2381	0,13935	0,02494	-0,2214	0,0873	0,20646	-0,1716	-0,2541	-0,1008	1

Table 1B: Correlation matrix of all elements regardless the sampling area

	Rb	*Pb*	*K*	*P*	*Sr*	*Y*	*Ga*	*Ti*	*Mn*	*As*	*Sn*	*Zn*	*Cu*	*Ni*	*V*	*Cr*	*Si*	*Al*	*Fe*	*S*	*Sb*	*Ca*	*Na*	*Mg*
Rb	1																							
Pb	0,367721569	1																						
K	0,514415991	-0,0236	1																					
P	-0,16731648	-0,1043	0,09974	1																				
Sr	-0,21548561	0,35552	-0,3829	-0,1892	1																			
Y	0,109882771	-0,1173	0,82749	0,21897	-0,3948	1																		
Ga	0,295264441	-0,0736	0,91194	0,13555	-0,4189	0,9229	1																	
Ti	0,366261705	-0,0438	0,91709	0,17271	-0,4196	0,9052	0,98769	1																
Mn	-0,22213374	-0,0821	0,03802	0,49494	0,10199	0,17814	-0,1055	-0,1238	1															
As	-0,1242178	-0,0116	0,09803	-0,0352	0,06067	0,07179	-0,1328	-0,1667	0,72346	1														
Sn	-0,18209266	-0,146	0,07141	0,04242	-0,1371	0,15233	0,17038	0,11945	0,08141	0,07651	1													
Zn	-0,24226924	-0,0999	0,49338	0,01905	-0,3325	0,67753	0,66552	0,5826	0,08377	0,22936	0,42023	1												
Cu	-0,16129788	-0,1884	0,59662	0,12963	-0,116	0,65654	0,54962	0,51038	0,47853	0,65956	0,35451	0,73261	1											
Ni	-0,04840973	-0,1325	0,36965	0,00875	-0,1238	0,58071	0,49665	0,47705	0,10188	0,05746	-0,2434	0,39933	0,3348	1										
V	0,504510872	-0,0201	0,97043	0,02825	-0,4246	0,81838	0,93829	0,92598	-0,0644	0,03227	0,16863	0,59515	0,5752	0,37363	1									
Cr	-0,04839983	-0,156	0,10376	-0,1527	-0,2118	-0,0074	0,12993	0,05504	-0,0418	0,29708	0,55342	0,57339	0,41441	-0,0454	0,2719	1								
Si	0,319830763	-0,1639	0,30039	0,25952	-0,7227	0,25191	0,33822	0,36642	-0,1697	-0,351	0,04859	0,1435	-0,1389	0,00397	0,29849	-0,0452	1							
Al	0,324848332	-0,0743	0,92307	0,16265	-0,4057	0,90234	0,9916	0,99458	-0,1222	-0,1387	0,14348	0,61311	0,55187	0,48118	0,93558	0,10132	0,33214	1						
Fe	-0,03510102	-0,2013	0,75394	0,37279	-0,387	0,93949	0,88226	0,86653	0,12031	-0,0671	0,07283	0,62264	0,56075	0,51259	0,71888	-0,1077	0,31886	0,86603	1					
S	0,580190537	0,86152	-0,0844	-0,3872	0,35978	-0,3502	-0,2144	-0,1761	-0,2971	-0,1153	-0,1793	-0,3769	-0,4213	-0,2249	-0,0725	-0,1361	-0,2097	-0,2071	-0,4636	1				
Sb	-0,20867499	-0,0379	-0,1083	-0,0152	0,22795	-0,1277	-0,0943	-0,1281	-0,0006	0,18117	0,22077	0,17179	0,21983	-0,249	-0,0582	0,42786	-0,0744	-0,0942	-0,0791	-0,1783	1			
Ca	-0,33280008	0,14404	-0,6271	-0,3482	0,7307	-0,6108	-0,6824	-0,6991	0,08382	0,27447	-0,0908	-0,3949	-0,164	-0,2191	-0,6171	0,02408	-0,9082	-0,6753	-0,6608	0,27975	0,10896	1		
Na	0,405159113	-0,0285	0,76018	0,30925	-0,3972	0,66911	0,8022	0,81707	-0,2058	-0,4222	-0,1609	0,25133	0,1228	0,37141	0,7398	-0,2053	0,51102	0,81964	0,72127	-0,1118	-0,2247	-0,7467	1	
Mg	-0,05583336	0,04609	0,17488	0,34642	-0,0794	0,1098	0,1791	0,11388	0,12371	-0,109	-0,3285	0,15579	-0,061	0,16103	0,17707	-0,0228	0,10449	0,14476	0,2342	-0,0542	-0,2376	-0,2082	0,47413	1

Table 2B: Correlation matrix for the samples collected from Hymettus area

	Rb	*Pb*	*K*	*P*	*Sr*	*Y*	*Ga*	*Ti*	*Mn*	*As*	*Sn*	*Zn*	*Cu*	*Ni*	*V*	*Cr*	*Si*	*Al*	*Fe*	*S*	*Sb*	*Ca*	*Na*	*Mg*
Rb	1																							
Pb	0,28047	1																						
K	0,99706	0,3202	1																					
P	0,64589	0,50486	0,63382	1																				
Sr	-0,3402	-0,3002	-0,3459	-0,4191	1																			
Y	0,81592	0,42671	0,81194	0,92737	-0,4832	1																		
Ga	0,90099	0,41209	0,90683	0,68852	-0,4846	0,7746	1																	
Ti	0,90112	0,47172	0,91147	0,74713	-0,4546	0,82021	0,97744	1																
Mn	0,37527	0,42341	0,37353	0,80286	-0,01	0,70578	0,43419	0,47045	1															
As	-0,1877	-0,1654	-0,1748	-0,3744	-0,0391	-0,2746	-0,3377	-0,3434	-0,2528	1														
Sn	-0,2381	-0,5673	-0,2543	-0,3915	0,44292	-0,3922	-0,3068	-0,2597	-0,2969	0,1267	1													
Zn	0,72785	0,34422	0,73852	0,56636	-0,4524	0,63342	0,92657	0,8654	0,46969	-0,3066	-0,2133	1												
Cu	0,79236	0,07002	0,8094	0,25294	-0,439	0,52334	0,76137	0,72885	0,05556	0,10936	-0,0188	0,72505	1											
Ni	0,47142	0,8255	0,51028	0,43296	-0,3861	0,41193	0,71286	0,70233	0,3419	-0,2463	-0,4036	0,74515	0,42486	1										
V	0,95046	0,51168	0,95954	0,77223	-0,4314	0,88841	0,9314	0,95383	0,50519	-0,2961	-0,3929	0,77113	0,69264	0,63705	1									
Cr	0,21318	0,75409	0,26223	0,0762	-0,2213	0,0378	0,41964	0,42393	0,00219	-0,0143	-0,3118	0,42916	0,22043	0,86799	0,36691	1								
Si	0,5905	0,39385	0,59079	0,87805	-0,4746	0,80504	0,77542	0,81032	0,74275	-0,3239	-0,2267	0,77434	0,40777	0,54289	0,71547	0,2029	1							
Al	0,78837	0,37727	0,79474	0,58867	-0,3946	0,62353	0,96292	0,93098	0,38648	-0,3823	-0,157	0,95385	0,70179	0,75896	0,82072	0,4943	0,76272	1						
Fe	0,59359	0,36199	0,5938	0,57262	-0,3868	0,53779	0,85235	0,78155	0,50148	-0,3898	-0,1809	0,95648	0,52884	0,75054	0,65617	0,44025	0,77775	0,92856	1					
S	-0,4982	-0,3869	-0,4891	-0,6455	0,18506	-0,5152	-0,7001	-0,6806	-0,5429	0,47262	0,36192	-0,6604	-0,2767	-0,5621	-0,562	-0,2686	-0,7136	-0,7319	-0,7413	1				
Sb	-0,0893	-0,0446	-0,0435	-0,3064	-0,0021	-0,1234	-0,1998	-0,1734	-0,0901	0,78659	-0,0595	-0,1582	0,2383	-0,1086	-0,1127	0,08401	-0,1874	-0,2793	-0,3473	0,42275	1			
Ca	-0,6658	-0,4234	-0,6701	-0,8091	0,49083	-0,7646	-0,877	-0,8813	-0,6618	0,33948	0,24749	-0,8914	-0,5222	-0,6702	-0,7737	-0,3452	-0,9718	-0,8857	-0,8893	0,75947	0,20454	1		
Na	-0,1497	-0,0252	-0,1456	-0,0356	-0,1026	-0,197	0,24023	0,17629	0,03603	-0,2938	0,25038	0,4891	0,05369	0,38804	-0,0891	0,32461	0,36669	0,4699	0,62976	-0,414	-0,3048	-0,4526	1	
Mg	0,01003	0,0611	0,01873	-0,0262	-0,1661	-0,1351	0,38646	0,29946	0,01303	-0,2612	0,15619	0,61844	0,22169	0,52981	0,05318	0,45887	0,37099	0,60095	0,7302	-0,466	-0,2706	-0,5042	0,96926	1

Table 3B: Correlation matrix for the samples collected from Tourkovounia area

APPENDIX E – DENDROGRAMS

Dendrograms from Hymettus area

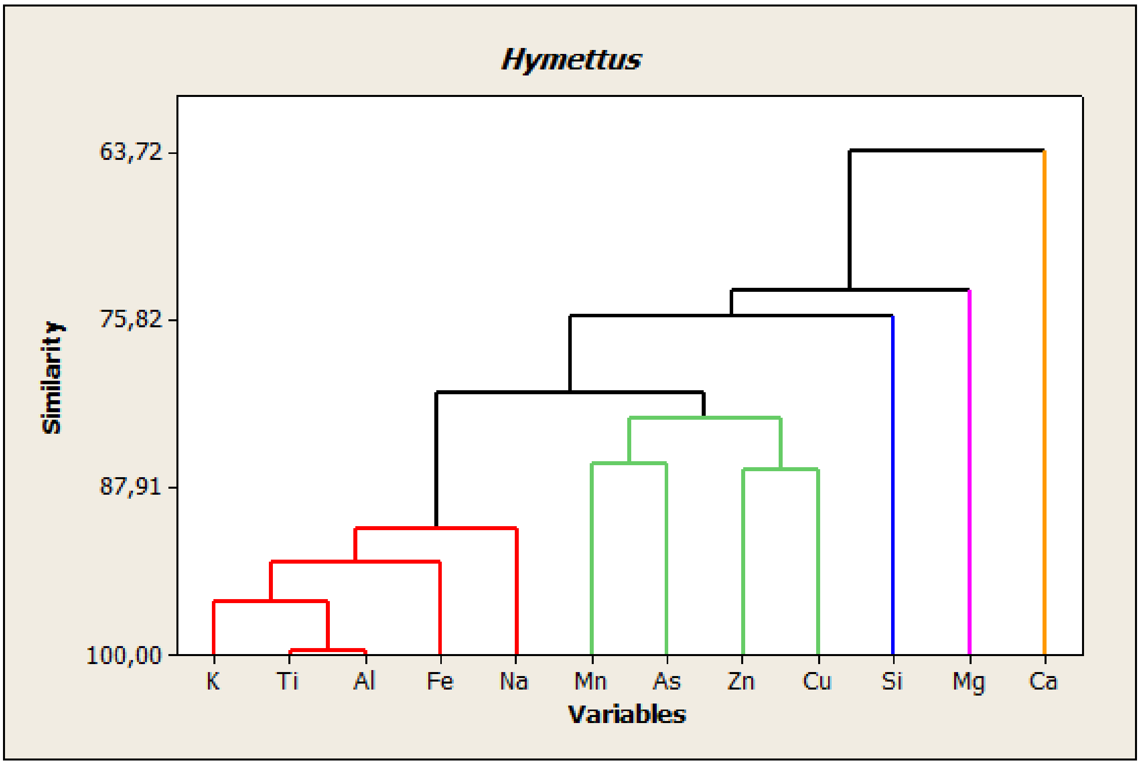

Figure 1E: Dendrogram for Hymettus area

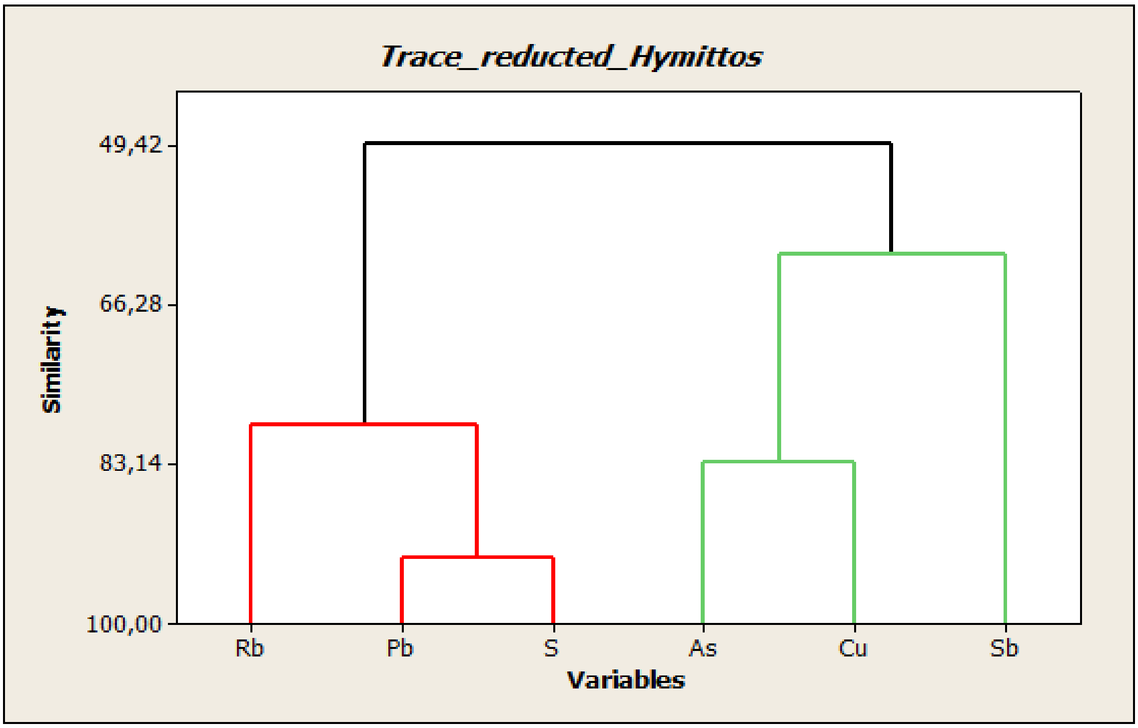

Figure2E: Dendrogram for trace elements from Hymettus area

Dendrograms from Tourkovounia area

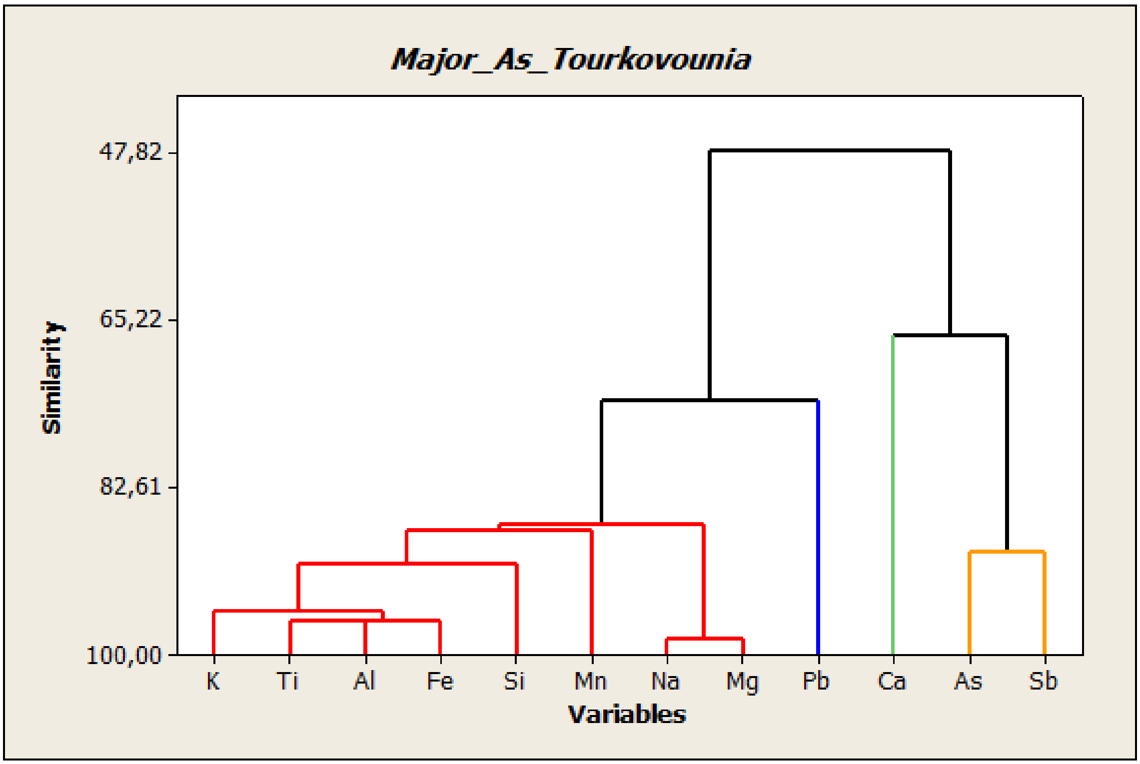

Figure 3E: Dendrogram for Tourkovounia area for most major and trace elements

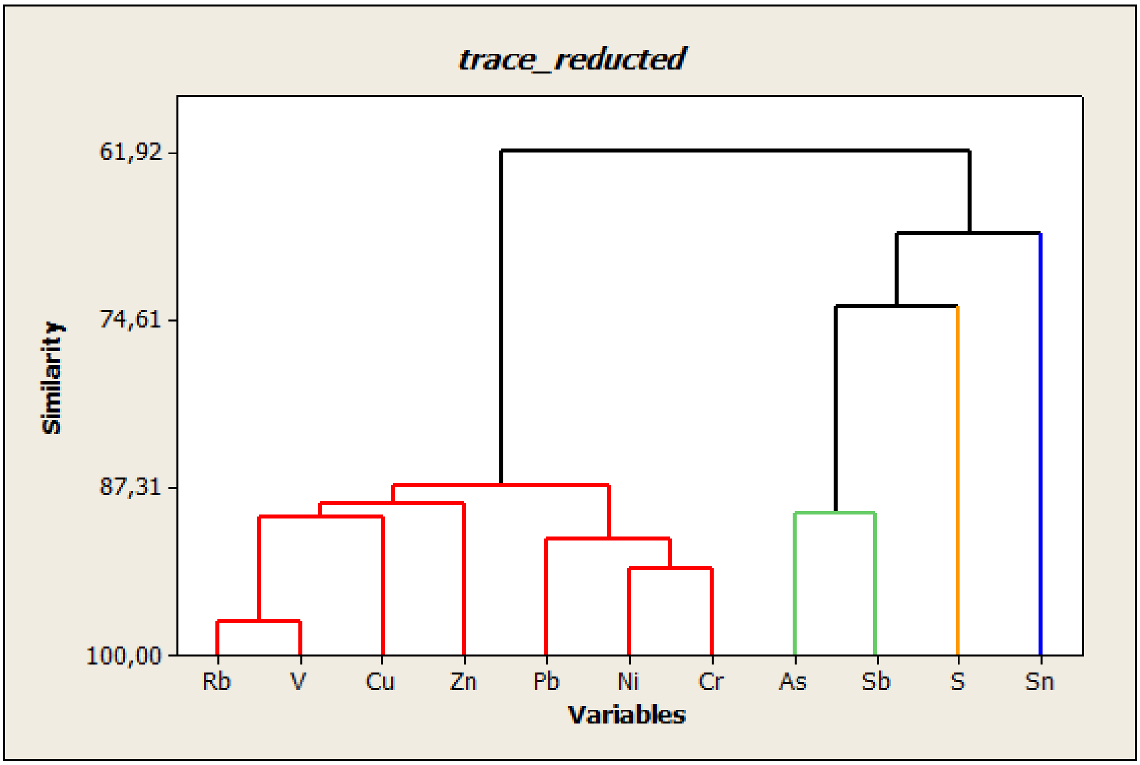

Figure 4E: Dendrogram from Tourkovounia area for all the trace elements

Dendrograms from Aigaleo area

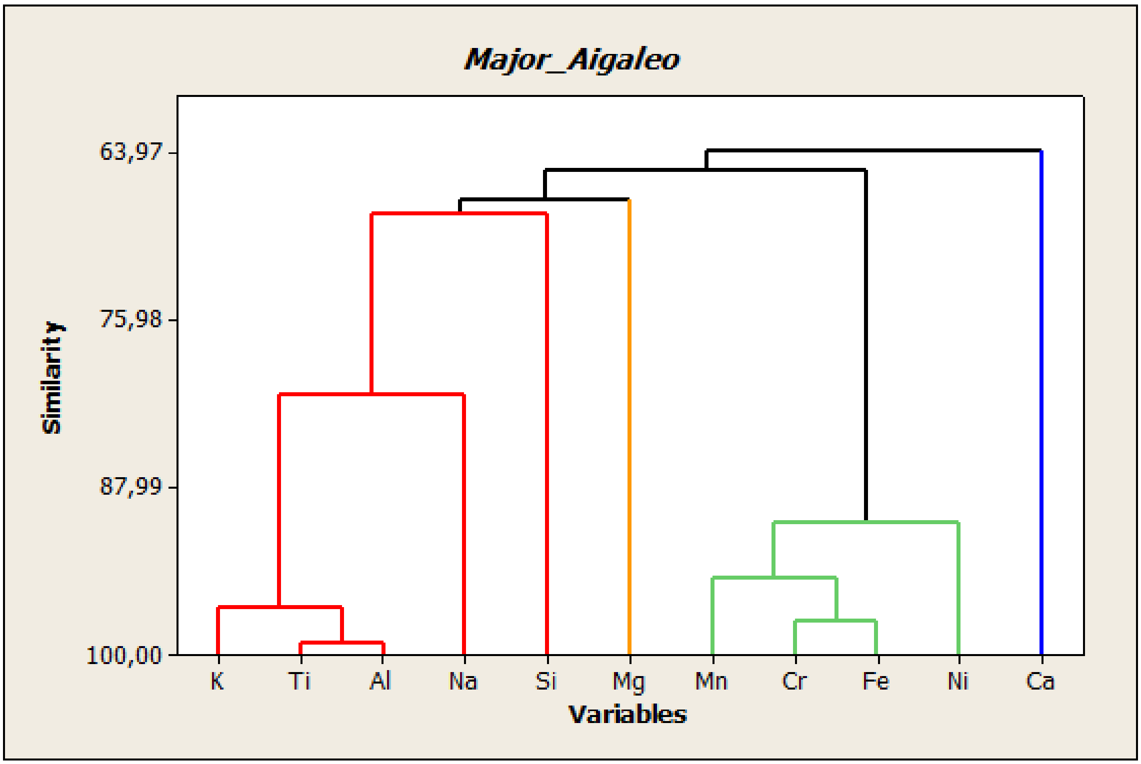

Figure 5E: Dendrograms for all the major elements from Aigaleo area

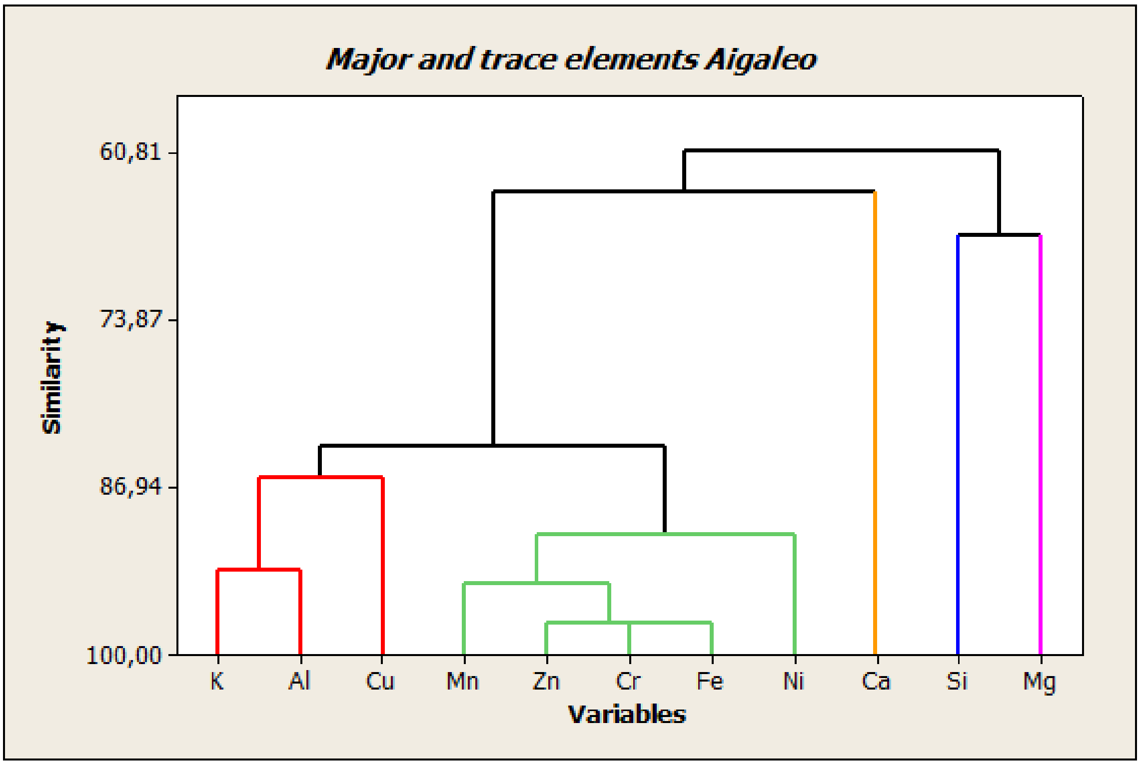

Figure 6E: Dendrograms for most major and trace elements from Aigaleo area