

Research Paper***Correspondence to:**

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APPLICATION OF NEAR-INFRARED SPECTROSCOPY FOR THE MINERALOGICAL IDENTIFICATION OF ROCKS FROM KOS ISLAND, AEGEAN SEA, GREECEMaria Kokkaliari^{1*}, Ioannis Iliopoulos¹¹Department of Geology, University of Patras, 2650 Patras, Greece,kokkaliari_m@upnet.gr morel@upatras.gr**Abstract**

Near-Infrared spectroscopy (NIR) is a useful tool for direct and on-site identification of rock mineralogy in spite of the difficulties arising in spectral evaluation, due to limited availability of spectral libraries at the time. Especially in the field, a functional methodology for the identification and evaluation if possible, of the geologic materials, is of interest to many researchers. However, several different parameters (such as grain size, color, mineralogy, texture, water content etc.) can affect the spectroscopic properties of the samples resulting in spectral variability. The subject of the present work focuses in various lithotypes (monzodiorite, diorite, altered diorite, actinolite schist, cataclasite, slate) from Kos Island, Aegean Sea, in Greece, all bearing hydrous minerals in various amounts. The evaluation of the results obtained from NIR spectroscopy offered important qualitative information about the mineralogy of the lithotypes examined. The important asset of the method is that no sample preparation was necessary. From the reflectance spectra, the NIR-active minerals that were identified include chlorite, micas, amphiboles and epidotes. Petrographic and mineralogic analyses were also employed in order to confirm the NIR results and provide more detailed information about the mineralogy of the samples, the grain size and the orientation of the minerals. Correlation of wavelength positions at ~1400 nm with loss on ignition (LOI) values led us to relate the various lithotypes in terms of their petrological affinities. NIR spectroscopy was proved to be a useful tool, especially for the mineralogic identification of rocks underwent low- to medium grade metamorphism, from greenschist to amphibolite facies.

Keywords: Near Infrared Spectroscopy, Kos Island, petrography, mineralogy, hydrous minerals

Περίληψη

Η Φασματοσκοπία Εγγύς Υπερύθρου (Near Infrared Spectroscopy – NIR) αποτελεί εξαιρετική μέθοδο για άμεση και υπαίθρια παρατήρηση, παρά τις δυσκολίες που προκύπτουν κατά την αξιολόγηση των φασματοσκοπικών υπογραφών λόγω της μέχρι σήμερα περιορισμένης διαθεσιμότητας φασματικών βιβλιοθηκών. Ειδικότερα, κατά την έρευνα πεδίου η χρήση λειτουργικής μεθοδολογίας για την αναγνώριση, ακόμα και αξιολόγηση αν αυτό είναι δυνατό, των γεωλογικών υλικών, αποτελεί αντικείμενο ενδιαφέροντος αρκετών ερευνητών. Ωστόσο, πολλές διαφορετικές παράμετροι (το μέγεθος των κόκκων, το χρώμα, η ορυκτολογική σύσταση, η υφή, η περιεκτικότητα σε νερό κλπ.) επηρεάζουν ποικιλοτρόπως τις φασματικές ιδιότητες των δειγμάτων με αποτέλεσμα την φασματική μεταβλητότητα. Αντικείμενο της παρούσας έρευνας αποτέλεσε μια ποικιλία λιθολογιών (μονζοδιορίτης, διορίτης, εξαλλοιωμένος διορίτης, ακτινολιθικός σχιστόλιθος, κατακλασίτης, αργιλικός σχίστης), από την νήσο Κω, στο Αιγαίο Πέλαγος, στην Ελλάδα, κοινό χαρακτηριστικό των οποίων είναι η παρουσία ένυδρων ορυκτών φάσεων σε διαφορετικές αναλογίες. Η αξιολόγηση των αποτελεσμάτων που προέκυψαν μέσω της εφαρμογής της φασματοσκοπίας NIR προσέφερε σημαντικές ποιοτικές πληροφορίες σχετικά με την ορυκτολογική σύσταση των υπό εξέταση λιθολογιών. Το σημαντικότερο πλεονέκτημα της μεθόδου είναι η μη αναγκαιότητα προετοιμασίας ειδικού τύπου παρασκευασμάτων για τα προς ανάλυση δείγματα. Στα φάσματα που αξιολογήθηκαν, τα ενεργά ορυκτά στην περιοχή εγγύς υπερύθρου του ηλεκτρομαγνητικού μήκους κύματος περιλαμβάνουν τους χλωρίτες, τους μαρμαρυγίτες, την ομάδα του επιδότου και τις αμφιβόλους. Πραγματοποιήθηκε επίσης πετρογραφική και ορυκτολογική ανάλυση ώστε να επιβεβαιωθούν τα αποτελέσματα που προέκυψαν από την χρήση της μεθόδου NIR και να παραχθούν λεπτομερείς πληροφορίες σχετικά με την ορυκτολογική σύσταση των δειγμάτων, το κοκκομετρικό τους μέγεθος και τον προσανατολισμό των ορυκτών. Η συσχέτιση των θέσεων απορρόφησης στα ~1400 nm με τις τιμές των απωλειών πύρωσης (Loss On Ignition – LOI), οδήγησαν στην συγκριτική ταξινόμηση των διαφορετικών λιθολογιών όσον αφορά το πετρολογικό τους υπόβαθρο. Η φασματοσκοπία NIR αποδείχθηκε χρήσιμη μέθοδος, ειδικά για την ορυκτολογική αναγνώριση των λιθολογιών που υπέστησαν χαμηλού έως μέτριου βαθμού μεταμόρφωση, από την πρασινοσχιστολιθική έως την αμφιβολιτική φάση μεταμόρφωσης.

Λέξεις κλειδιά: Φασματοσκοπία Εγγύς Υπερύθρου, Κως, πετρογραφία, ορυκτολογία, ένυδρα ορυκτά

1. INTRODUCTION

In the present study, a variety of different rock samples from Kos Island, South-East Aegean characterized by the presence of various amounts of hydrous minerals, were used to acquire reflectance spectra in the near infrared (NIR) electromagnetic spectral region. The absorption features obtained are a result of energy-matter interactions caused by molecular vibrations at specific frequencies. The evaluation of these features allows us to determine which functional molecular group participates in the structure of the mineral. The major spectral features in the NIR region are a result mostly of the water content and the vibrations of the hydroxyl groups such as Al-OH, Fe-OH, Mg-OH (Clark et al., 1990). We attempt to examine the spectral characteristics of the different lithotypes and the way that the mineralogy possibly affects the absorption features recorded in each spectrum obtained. The spectroscopic analysis is supported by the petrographic study coupled with photomicrography and X-Ray Powder Diffraction (XRPD) analysis, aiming to verify the mineralogical composition of the studied samples and classify them into the main rock types.

2. GEOLOGICAL SETTING

Kos Island is part of the Dodecanese and located in the eastern edge of the Aegean Volcanic Arc (Pe-Piper and Piper, 2005). The geologic structure of the island is composed of various lithologies (Fig. 1) spanning the three main categories of rock classification: igneous (plutonic rocks with monzodioritic composition, dacitic to rhyolitic volcanic rocks and pyroclastic deposits), metamorphic (hornfels due to contact metamorphism, amphibolites, slates, marbles, metavolcanics) and sedimentary rocks (Quaternary sediments and marine and lacustrine deposits) (Kalt et al., 1998; Altherr and Siebel, 2002; Drinia et al., 2010; Soder et al., 2016).

Significant events for the petrologic evolution of Kos were the two magmatic episodes occurred in the area; they are mainly observed in the western part of the island and dated at ~ 3.5 Ma and ~ 161 ka, respectively (Altherr et al., 1976; 1982; Gralla, 1982; Dürr, 1986; Jacobshagen, 1986; Henjes-Kunst et al., 1988; Kalt et al., 1998; Altherr and Siebel, 2002; Pe-Piper and Piper, 2002). The latter one (the ~161 ka event) caused the largest Quaternary eruption (>60 km³) ever affected the Mediterranean and led to the formation of the voluminous, unwelded Kos Plateau Tuff (KPT; Allen, 2001).

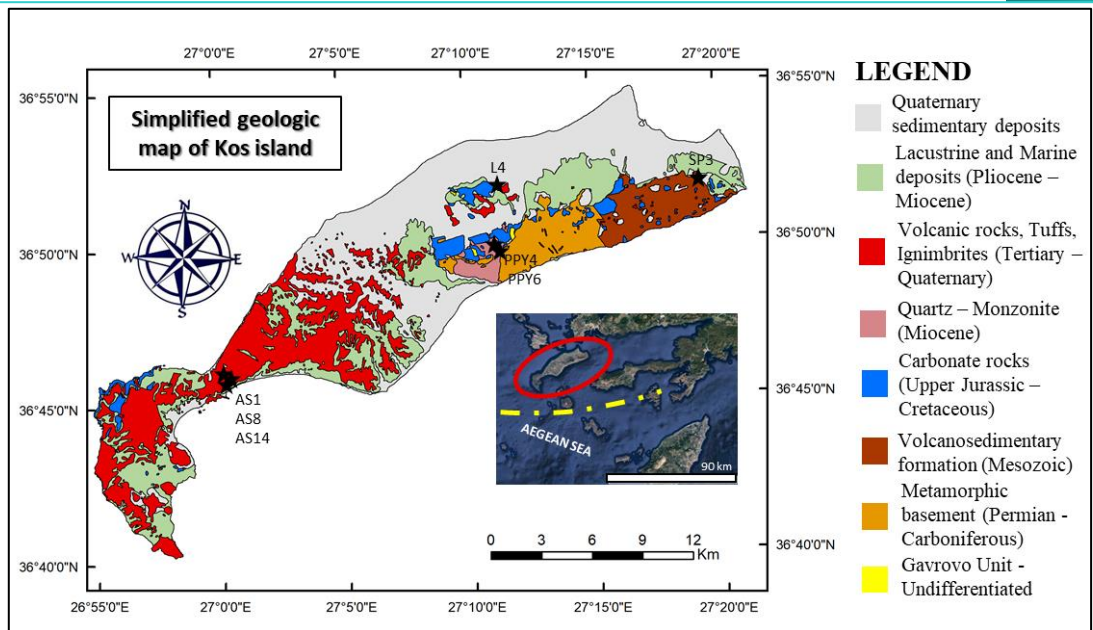


Fig. 1: Simplified geologic Map of Kos Island, Eastern Aegean Sea, Greece modified after Triantaphyllis (1994, 1998).

3. MATERIALS AND METHODS

Sampling was performed on Kos in 2016 and comprised a range of different lithologies: actinolite schist, slate, cataclasite, monzodiorite, diorite, and altered diorite, which are characterized by the presence of hydrous minerals. Petrographic thin sections were prepared and studied by means of transmitted light microscopy (Zeiss AxioScope A.1) in order to determine the rock type and mineral mode. The detailed petrographic analysis provided additional information for the texture of the samples and their particle size, whilst led us to infer about the metamorphic conditions of the metamorphosed rocks. The mineralogy of the samples was further verified by means of X-Ray Powder Diffraction (BRUKER D8 Advance) using Ni filtered Cu-K α radiation, operating at 40 kV and 40 mA and employing a Bruker Lynx Eye fast detector. Samples were step-scanned from 2° to 70° 2 θ and a time/step of 0.2 s. Samples were powdered (< 10 μ m) in a vibration disc mill using an agate grinding set and randomly mounted in a sample holder. The crystalline phases were identified using the DIFFRACplus EVA software (Bruker-AXS, USA), based on the ICDD Powder Diffraction File (2006 version). The reflectance spectroscopy (SM-3500 Spectral Evolution portable spectrometer) was applied on carefully selected, smooth, unaltered surface of the hand specimens, bringing the mineral probe spectrometer in contact with the surface of the samples. The data acquired ranges from 0.35 to 2.5 μ m with a spectral resolution according to the software, between 3 and 8 nm. The spectra were finally produced by the instrument at 1 nm intervals, using the DARWin SP

Data Acquisition software, which is accompanied by the United States Geological Survey (USGS) mineral standards database. Sample spectra were first calibrated relative to a Spectral Evolution standard panel. The samples were not pre-processed in order to simulate as much as possible the realistic conditions in the field. Loss on ignition values of the samples were also determined by the weight difference after drying the sample powders at 105°C overnight and igniting them at 1050°C for three hours. All analyses described above were performed in the Research Laboratory of Minerals and Rocks, Department of Geology, University of Patras, Greece.

4. PETROGRAPHIC AND MINERALOGICAL ANALYSIS

The Koan rock samples considered in the present study were characterized through their petrographic examination and their mineralogical composition was semi-quantified by means of XRPD analysis. Sample PPY4 is inequigranular, coarse-grained with porphyroid, poikilitic texture, comprising anhedral quartz (~2 vol %; <0.3 mm) and euhedral to subhedral plagioclase (~33 vol %; <5 mm) and alkali-feldspar (~20 vol %; <7 mm). Euhedral to subhedral hornblende (~35 vol %; <4 mm), biotite (~10 vol %; <1mm), and sphene (~1 vol%; up to 3mm) are also included in the mineralogy of the sample, as well as minor opaque minerals (<1 vol %). Hornblende was characterized by twinning and was often pseudomorphically replaced by biotite (Fig. 2A), occasionally altered to chlorite. The petrographic characteristics of the sample indicate a monzodioritic plutonic rock, where the presence of myrmekite i.e., a secondary texture including irregular, vermicular intergrowths of quartz in plagioclase, commonly in contact with alkali-feldspar crystals, and perthite (Fig. 2B), i.e., exsolved lamellae of plagioclase in an alkali-feldspar crystal, were also observed. Sample PPY6 (Fig. 2C), has similar petrographic characteristics with the sample PPY4, but biotite (~30 vol %) and hornblende (~32 vol %) are prevailing in respect to the rest of the minerals (quartz: ~2.5 vol %; alkali-feldspars: ~10 vol %; plagioclase: ~25 vol %;) indicating a more dioritic composition. The grain size of the minerals varies i.e. quartz up to 0.2 mm; plagioclase up to 4 mm; alkali-feldspars up to 8 mm; hornblende up to 5 mm and biotite up to 3 mm. The predominant mineral in samples AS1 and AS8 is subhedral to anhedral actinolite (70-75 vol %), whilst minor subhedral hornblende (~1 vol %), forming coarse-grain phenocrysts (up to 6 mm) in a fine-grained matrix with plagioclase (10-15 vol %), and its saussuritization products epidote - zoisite (10-12 vol %), chlorite (1-3 vol %). Minor anhedral quartz (<1 vol %) (Fig. 2D) completes the studied mineralogical assemblage. They are low grade metamorphic lithotypes after a dioritic protolith as observed macroscopically on the hand samples, characterized by inequigranular, grano-nematoblastic texture.

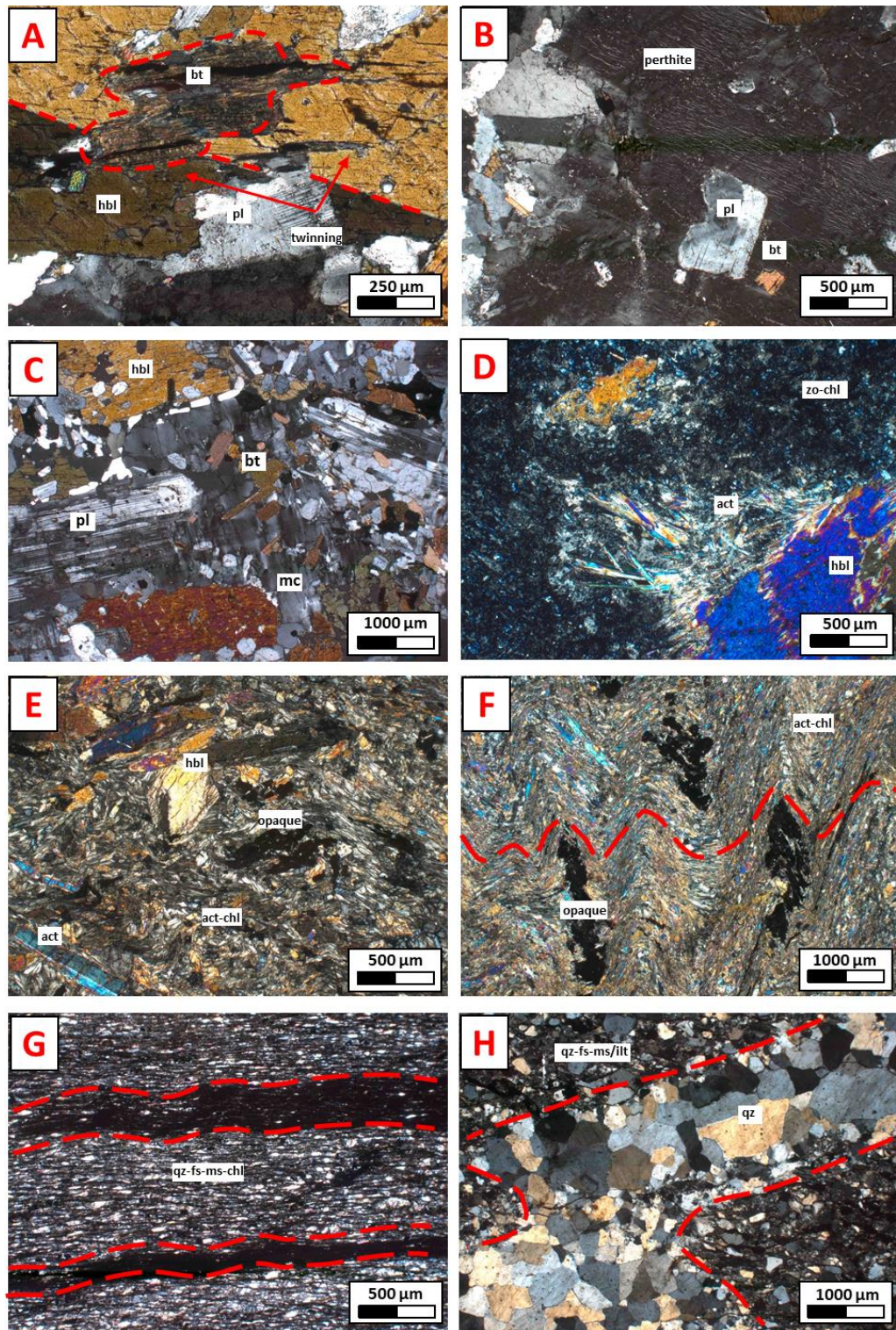


Fig. 2: Representative photomicrographs of the studied samples: (A, B) monzodiorite (sample PPY4); (C) altered diorite (sample AS1); (D) diorite (sample PPY6); (E, F) actinolite schist (sample AS14); (G) slate (sample L4); (H) cataclasite (sample SP3). All photomicrographs are captured under cross polarized Nicols (XP). Mineral abbreviations are according to Whitney and Evans (2010).

The amphiboles often appeared with tectonic twinning, king-band and consertal textures. The sample was characterized by secondary growth of veins rich in

plagioclase and zoisite. The sample AS14 has a grano- lepto/nemato-blastic texture (Fig. 2F), comprising mainly actinolite (~65 vol %), and minor hornblende (~2 vol %), where the average grain-size of the amphiboles is 1 mm, and fine-grained plagioclase porphyroblasts (~8 vol %) in a chlorite-rich (~19 vol %) matrix. Fine-grained anhedral quartz (~4 vol %) was also detected. Due to the presence of hornblende (Fig. 2E) it can be deduced that the actinolite schist was metamorphosed at upper greenschist to lower amphibolite facies. According to the mineralogy of the sample, the protolith is probably a mafic igneous rock, metamorphosed in low to medium grade conditions, forming an actinolite schist. The presence of yellowish areas represents oxidized biotite and its alteration product, chlorite. Intense foliation was observed in the macroscopic samples, characterizing the orientation of the fibrous minerals.

Sample L4 is fine-grained, i.e. the average size of the crystals is < 100 µm, and has a grano-nematoblastic texture comprising chlorite (~42 vol %), muscovite (~36 vol %), quartz (~12 vol %) and plagioclase (~8 vol %) and minor alkali-feldspar (~2 vol %). The sample is characterized of orientation of the grains due to metamorphism and the presence of micro-foliations and micro-fractures. Micro-layers richer in recrystallized micro/crypto-crystalline micas (Fig. 2G) are also observed in the petrographic analysis. The textural characteristics and the mineralogy of the sample are characteristic of a slate, a pelitic protolith that has undertaken low grade metamorphism (chlorite zone according to Barrow-type metamorphism). Sample SP3 has similar mineralogy to L4 (i.e. the slate), consisting of quartz (~65 vol %), plagioclase (~20 vol %) and minor alkali-feldspars (<1 vol %) up to 0.5 mm, as well as fine-grained muscovite/illite (~9 vol %) and chlorite (~6 vol %) and differing however to the semi-quantification of the minerals as obtained through the XRPD results. The sample has a cataclastic texture, implying dynamic deformation, where the grains of the siliceous minerals being generally rounded, typical for cataclasites. Micro-brecciated zones and the secondary development of veins rich in coarse-grained quartz, were also observed (Fig. 2H).

5. THE APPLICATION OF NEAR INFRARED SPECTROSCOPY

The minerals that were recognized through the examination of the studied samples with Near Infrared Spectroscopy are, in accordance to the petrographic and mineralogic analysis, epidote, chlorite, amphiboles and micas (Fig. 3). As concluded from the spectroscopic analysis, the mineral abundances play an important role for

their identification. The major absorption features for each mineral identified through NIR are listed in Table 1.

Table 1. Major absorption features in the Near Infrared Spectroscopy (Clark, 1999).

<i>Position (nm)</i>	<i>Mechanism</i>	<i>Minerals identified</i>	<i>Diagnostic Absorption Features (nm)</i>
~ 1400	OH ⁻ and water	Actinolite	2314-2324, 2380-2390
~ 1900	Molecular water	Hornblende	2324-2350, 2390-2410
~ 2200	Al-OH	Epidote	1540, 1835, 2255, 2335-2342
~ 2250	Fe-OH Combinations	Chlorite	1400, 2250, 2350
~2300 - 2400	Mg-OH Combinations	Muscovite	2200, 2344, 2440
		Biotite	2250, 2340-2370, 2400

The NIR spectra of the altered diorites (samples AS1, AS8) are dominated by the absorption features of epidote and amphibole group (Fig. 4A). The small shoulder-like feature at 2257 nm in the AS1 spectrum is attributed to the Fe-OH absorption features of epidote (Clark et al., 1990), whereas the 2323 nm and 2390 nm absorption features are produced from the Fe-OH and Mg-OH molecular bonds in actinolite. No absorption features relative to hornblende were attested, possibly due to the low content of this mineral (~1 vol %) and consequently the overlapping features from the NIR-active minerals. In the spectrum of sample AS8, zoisite absorption features and specifically those at the 1660 and 1890, 2299 and 2349 nm are readily observed verifying the abundance of this mineral as was already recorded through the petrographic study and the mineralogical analysis. The main absorption features of amphiboles are rather poorly developed at the ~2320 and ~2390 nm region of the spectrum, exhibiting broad shape due to overlapping features.

The main spectral characteristics of epidote and chlorite overlap in the SWIR region and are not easily distinguished. Such difficulty has been previously described upon coexistence of the two minerals in the same sample (Dalton et al., 2004; Abweny et al., 2016). Chlorite in these cases participates only in small proportions in the AS1 and AS8 samples (1.5-3 vol %) and is not distinguishable.

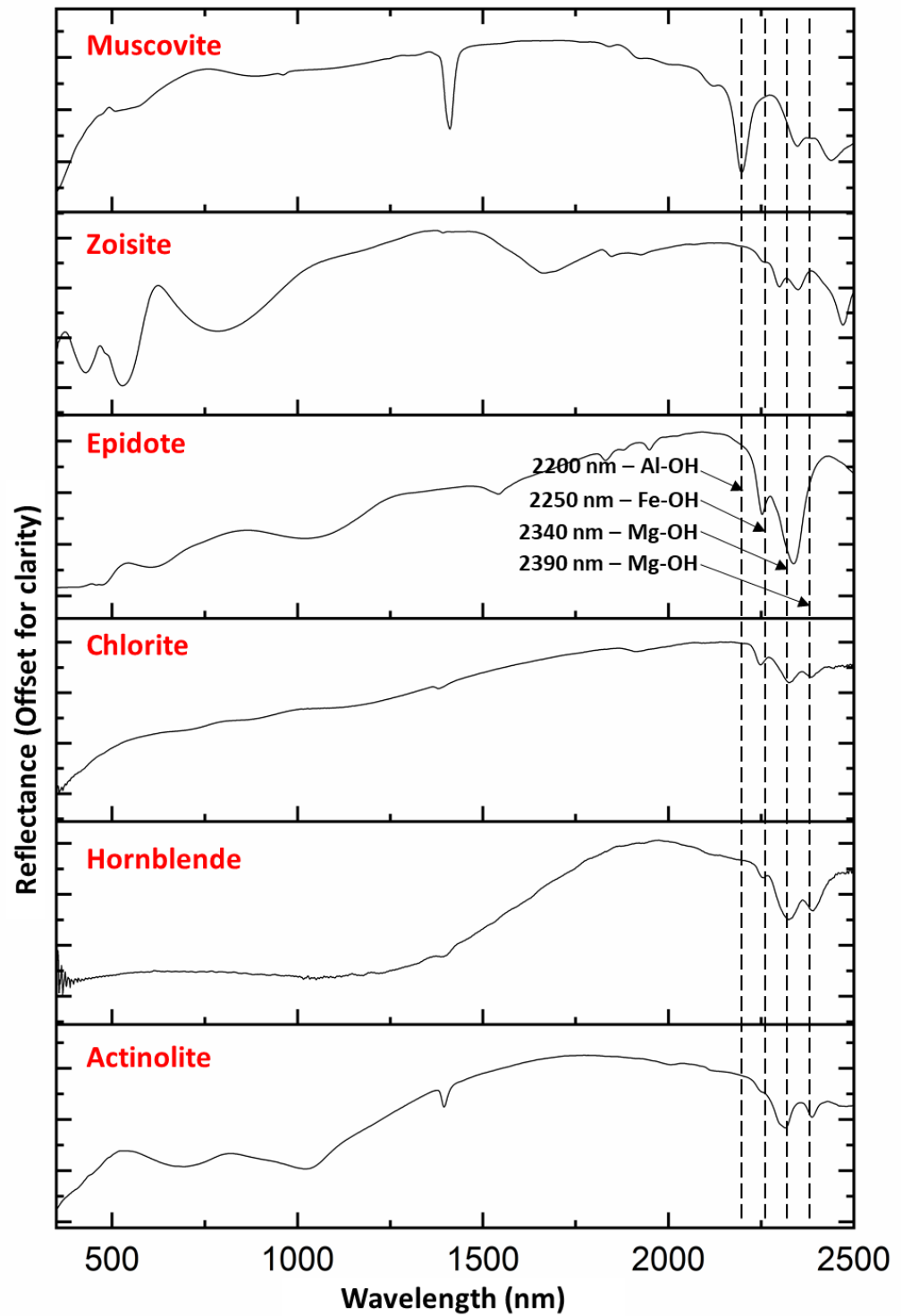


Fig. 3: Laboratory reference spectra of the USGS spectral library that were used in this research (Clark et al., 2007).

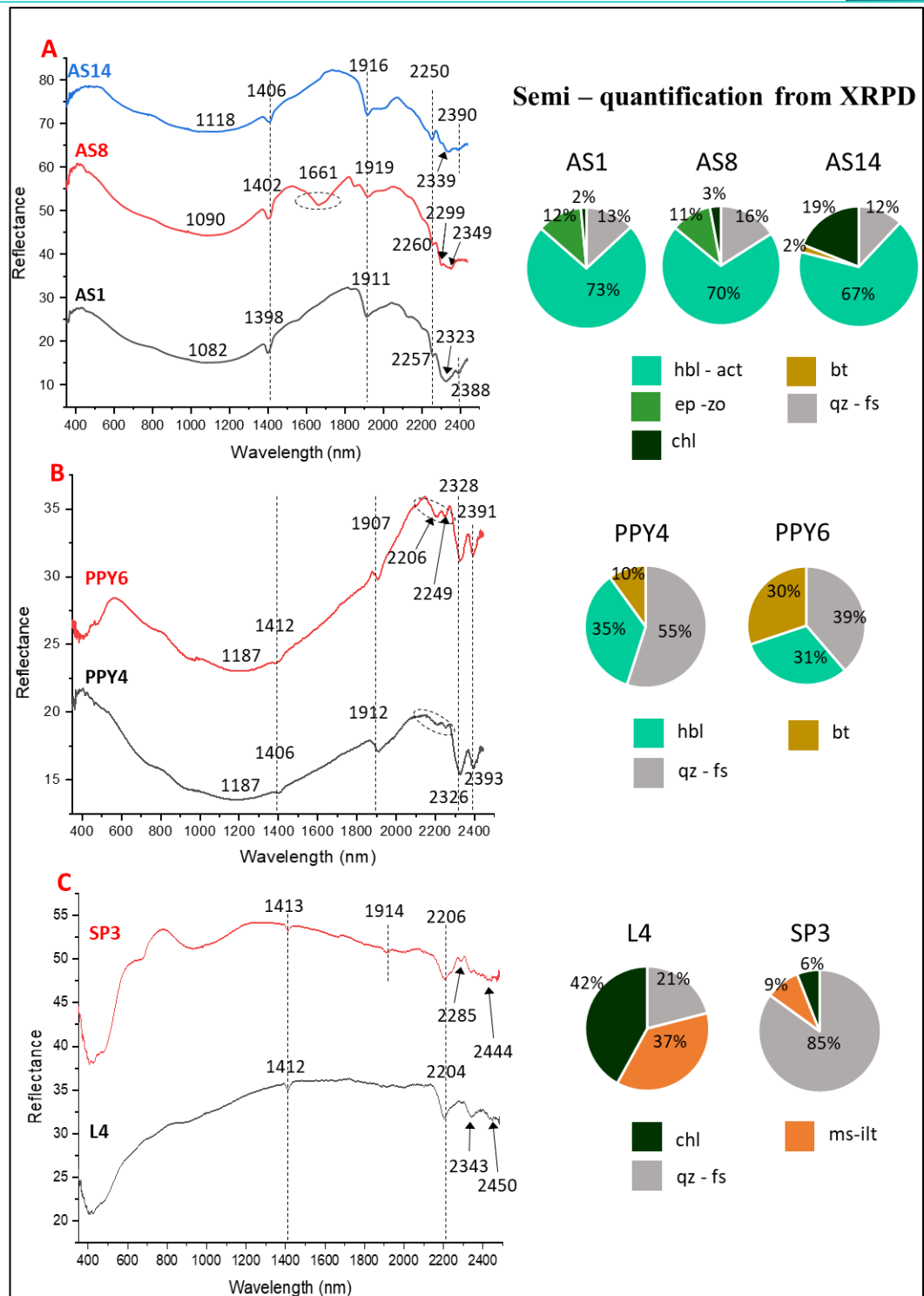


Fig. 4: Representative reflectance spectra of (on the left) and mineral semi-quantification pies (on the right) for the samples considered in the present study: (A) altered diorites and actinolite schist; (B) monzodiorite and diorite; (C) slate and cataclastite. Mineral abbreviations are according to Whitney and Evans (2010).

The actinolite schist spectrum (sample AS14) is characterized mainly by the absorption features (Fig. 3A) of chlorite at 2249 and 2339 nm. The absorption features of actinolite are rather subdued (absorption features at ~2320 and ~2390 nm),

due to overlapping absorption features of the coexisting chlorite, similarly to what has been reported by Abweny et al. (2016). The wavelength position of the absorption features at 2249 and 2339 nm, indicates the presence of chlorite with intermediate chemical composition (Mg,Fe-chlorite), at transitional metamorphic conditions of greenschist to amphibolite facies (Abweny et al., 2016). Our petrographic study indicates the presence of actinolite and minor hornblende (~2 vol %), implying upper greenschist to lower amphibolite facies metamorphism. The sharp absorption at 2249 nm, except for chlorite, could be also attributed to biotite, however this mineral was not detected through XRPD analysis, even though it was identified in the petrographic study. Samples PPY4 (monzodiorite) and PPY6 (diorite) are coarse-grained and contain abundant hornblende, the presence of which is detected through the characteristic diagnostic doublet features at ~2330 and ~2390 nm in the relative reflectance spectra (Fig. 4B). The presence of biotite in both samples is attested by the characteristic features observed in the region of ~2250 nm, being more evident in sample PPY6 due to the higher content of biotite. Particularly, the small sharp absorption feature at 2249 nm caused by molecular vibrations of Fe-OH is indicative of this mineral. The small feature at 2206 nm represents Al-OH molecular vibrations, which possibly indicates the presence of clay minerals formed due to the alteration of biotite. Furthermore, the increased proportion of Fe due to the increased presence of biotite in PPY6 sample, inherits a positive slope to the spectrum, from 1400 to 2000 nm.

The spectra obtained from samples SP3 (cataclasite) and L4 (slate) are characterized by broad rounded absorption features at ~2200 nm and small features at ~1400 nm, indicating the presence of hydrous, Al-rich minerals, like muscovite (Fig. 4C). The slate spectrum (sample L4) is characterized by the characteristic absorption features of mica. The intense absorption feature at ~2200 nm, and the doublet features at 2342 nm and 2450 nm are diagnostic for muscovite and helps distinguishing it among other micas. Muscovite and illite have common spectral characteristics; their main difference however is the depth of the absorption around 1900 nm (Pontual et al., 1997; Dalm et al., 2014), relatively to the crystallinity of these minerals. Deep absorption features at 1900 nm indicate that water molecules occupy more interlayer sites in the crystal lattice, suggesting the presence of a lower crystalline illite rather than higher crystalline muscovite (Pontual et al., 1997). However, a more precise term for the calculation of the crystallinity of these minerals regarding the NIR spectroscopy is considered to be the 'NIR crystallinity' (Dalm et al., 2014), since different NIR crystallinities of white mica do not constitute discrete mineralogical groups *sensu stricto*. Since the absorption feature at ~1900 nm of sample L4 is almost

not developed, indicating a good 'NIR crystallinity' and in combination with the petrographic analysis, the presence of well crystalline mica was concluded, indicating typical muscovite. The absorption feature at 2342 nm is broad and deep and is an overlapping feature of muscovite and chlorite. The characteristic absorption features of phyllosilicate minerals in higher wavelengths (> 2300 nm) however, are subdued in the SP3 spectrum, and not distinct, due to their small percentage compared to the rest mineralogy as opposed to the siliceous minerals (quartz and feldspars). A small, sharp absorption feature at 2285 nm is identified, however the identification of the mineral is difficult to be determined. The presence of OH⁻ groups associated with octahedral sites occupied by Al and Mg causes absorption features from 2200 to 2300 nm (Hunt, 1977), however the absorption features around 2290 suggests the presence of Fe-OH bonds of nontronite (Clark et al. 1990).

6. DISCUSSION

Our study shows that each lithotype exhibits diagnostic spectra in the NIR region with common absorption features according to their mineralogy. Such features are significantly influenced by the percentage participation of the NIR-active minerals and their crystallinity. However, some minerals even if are easily identified through petrographic and mineralogical techniques (quartz and feldspars), were not recognized through NIR Spectroscopy. On the other hand, the presence of metallic minerals, even in trace amounts, seems to influence the visible range of the spectra. The minerals that were identified through the NIR spectroscopy in the present study are epidotes, amphiboles, micas and chlorites.

Even though Near Infrared Spectroscopy has potential for the identification of the minerals that belong to the same mineralogical group (e.g. actinolite-hornblende for amphiboles or the minerals of epidote group), the identification is complicated when more than three minerals comprise the mineralogic composition of the rock due to the presence of overlapping features (Abweny et al., 2016). However, it can be assumed that NIR spectroscopy can be a direct mean for qualitative mineralogical identification of the hydrous minerals bearing rocks in the field and it can be an extremely useful tool in cases of low amount of sample. In recent literature has been proven that NIR can be applied in metamorphic geology, on identification of hydrothermal or to distinguish the metamorphic grade of low to medium grade metamorphism i.e. greenschist to amphibolite facies alterations (Duke, 1994; Longhi et al., 2000; Herrmann et al., 2001; Sun et al., 2001; Doublier et al., 2010; Duke & Lewis, 2010; 2012; Ruitenbeek et al., 2012; Dalm et al., 2014; Abweny et al., 2016; Kamps et al.,

2018; Shi et al., 2018). According to Shi et al. (2018), spectral characteristics of glaucophane can be identified in the NIR region and consequently the blueschist metamorphism can be recognized. Yang et al. (2018) described that the wavelength position of the absorption features of chlorites are correlated with the Fe/(Fe +Mg) values. More specifically, the two diagnostic absorption features of chlorites i.e. at ~2250 and ~2240 nm, occur at higher wavelength positions for Fe-rich chlorites, and at lower wavelength positions for Mg-chlorites. The absorption feature at ~2340 nm proved to be an excellent tool for the discrimination of low grade metamorphic and hydrothermal chlorites (Kamps et al., 2018), indicating that the hydrothermal group have absorption features at higher wavelength. Furthermore, the NIR absorption features of chlorite of rocks metamorphosed in the amphibolite facies occur at lower wavelengths than rocks metamorphosed in the greenschist facies, which are directly dependent on the occurring metamorphic mineral assemblages (Abweny et al. 2016). The Al-OH shift of the absorption feature at ~2200 nm of micas allows us to determine and map regional metamorphic facies (Duke, 1994; Duke and Lewis, 2010; Van der Meer, 2018).

As is well known (Clark, 1999), NIR spectroscopy is extremely sensitive in the presence of water. In order to unveil this sensitivity, we tried to correlate our NIR results with the measurements of the loss on ignition (LOI). In this respect, the basic characteristic absorption features of OH⁻ at 1400 nm were used, because they were common absorption features to almost every spectrum acquired in the present study (Fig. 5). Since the mineralogical assemblages have been verified through the mineralogical analysis and no mineral with H₂O in its crystal structure was identified, the wavelength position of the absorption feature at ~1900 nm characterizes the presence of molecular water in the crystal structure of the minerals can be attributed either to hydration or trapping water in the crystal lattice. The exact wavelength position of this feature for the altered diorites (AS1, AS8) and the actinolite schist (AS8) ranges from 1398 to 1406 nm, whereas for the slate (L4) and the cataclasite (SP3) is observed at approximately 1412-1413 nm and for the monzodiorite (PPY4) and the diorite (PPY6) ranges from 1409 to 1412 nm. The samples SP3 (cataclasite), L4 (slate) and AS14 (actinolite schist) plot in different areas of the diagram whereas the rest of the samples are clustered in two distinct groups. The first group includes samples PPY4 and PPY6 (monzodiorite and diorite, respectively) and the second group includes samples AS1 and AS8 (altered diorites). This clearly indicates that different lithotypes occupy different areas of the diagram and the samples are differentiating according to their mineralogical assemblage and therefore to their genetic environment.

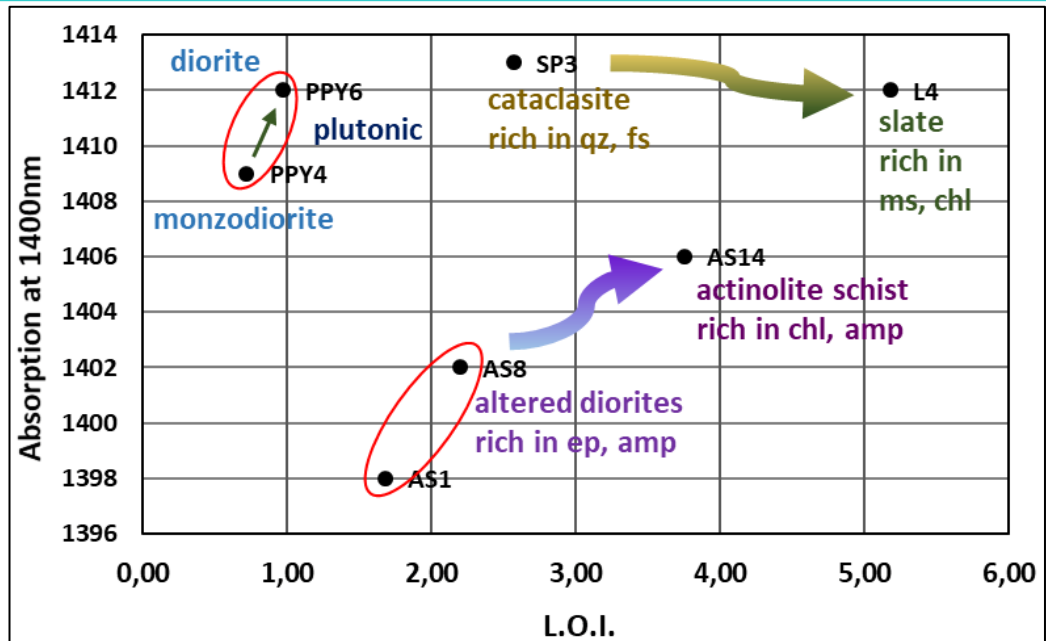


Fig. 5: Diagram with the LOI values plotted against the ~1400 nm absorption features.

7. CONCLUSIONS

Epidotes, chlorites, amphiboles and micas were the main spectrally identifiable minerals in the various lithotypes from Kos island examined in this study. Their absorption features in the NIR spectra were occasionally influenced by their content in each sample and the rest of the minerals present. The presence of minerals with common NIR absorption characteristics may cause overlapping features which hinder the interpretation of the rock mineralogy. Furthermore, some minerals such as quartz and feldspars that were readily identified by thin section and mineralogical analysis could not be easily detected with NIR. Their abundance however can influence the reflectance of the spectra, not the wavelength position of the absorptions. It should be mentioned that through the petrographic analysis, a variety of textural characteristics were observed, the influence of whom in the spectral characteristic of the samples is still debated (Sgavetti et al., 2007).

Our study shows that, in agreement with the literature, NIR spectroscopy can be a mean for a direct evaluation of the metamorphic grade especially in the field, and in cases of low amount of the sample, since no experimental preparation is needed. The recognized minerals observed in the present work constitute the main metamorphic minerals in greenschist to amphibolite facies. Epidotes and amphiboles are good indicators to evaluate the metamorphism that the rocks had experienced; however,

their spectral characteristics are influenced by the rest of the mineralogy and the relative mineral content. The spectral characteristics of altered diorites (samples AS1 and AS8) are clearly influenced by low grade metamorphism, as opposed to monzodiorite and diorite (samples PPY4, PPY6). Epidotes in the altered diorites are good reflectors for the NIR spectroscopy even though they are fine-grained, saussurization products, whereas the spectral characteristics of the amphiboles are broad and not always clearly distinguished. Moreover, the presence of zoisite influenced even more the characteristic absorption features of the spectrum (sample AS8). The spectrum of actinolite schist (sample AS14) is dominated by the chlorite and actinolite absorption features, where due to the abundance of chlorite in the sample, the characteristic absorption features of actinolite are obscured.

The spectral characteristics are in agreement with the literature, indicating a transition in the metamorphic conditions of greenschist to amphibolite facies and the presence of Mg,Fe-chlorite, with intermediate chemical composition. On the other hand, the absorption features of hornblende from the plutonic rocks (samples PPY4 and PPY6) dominates the spectral characteristics of these samples. The dioritic composition of the sample PPY6, followed by the higher percentage participation of biotite, compared to the sample PPY4, attributes more intense absorption features in the ~2250 nm region, and hence can be concluded that NIR spectroscopy have potential for distinguishing plutonic rocks with monzodioritic to dioritic composition. Slate (samples SP3) and cataclasite (sample L4) even though they have similar mineralogy, they differ in the mineral's percentage participation. This differentiation is also observed in the relatively spectra, where the abundance of quartz and feldspars in the cataclasite obscures the absorption features of muscovite-illite and chlorite whereas the spectrum of slate (sample L4) is characterized by well-defined absorption features, indicating that NIR spectroscopy can identify the low-grade metamorphism of pelitic protoliths.

Finally, the correlation of loss on ignition with the ~1400 nm wavelength position facilitates separation of unaltered plutonic samples (samples PPY4 and PPY6) from the altered ones (samples AS1 and AS8). The plot of the rest of the samples in different areas in the relative diagram is linked to their mineralogical composition, and hence their genetic environment. Further research is needed with a larger variety of samples in order to evaluate in detail the NIR potential as a petrologic tool for the genetic environment of the lithotypes.

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