





Differentiation of muscovites in igneous and metamorphic rocks according to their Raman spectra

Magmatik ve metamorfik kayalardaki muskovitlerin Raman spektrumlarına göre ayırımı

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Abstract

Muscovite is a dioctahedral mica mineral belonging to the phyllosilicates, also known as sheet silicates. It is also referred to as white mica; muscovites can be found in all major rock groups, including igneous, metamorphic, and sedimentary rocks. Muscovites, which are common in igneous rocks, especially in S-type granites and pegmatitic rocks, are also present in varying proportions within metamorphic rocks composed of schist and gneiss in the greenschist facies. Phyllosilicates, one of the main types of silicates, possess variable structures and complex chemistries. Due to these structural and compositional differences, the Raman shifts of phyllosilicates can be observed in different spectral regions. Furthermore, variations in the crystallization processes of magma and differences in the pressure-temperature conditions during metamorphism affect the intensity and wavenumber of their Raman spectra. In this study, the Raman spectra of muscovites of both igneous and metamorphic origins were compared, and the differences in their Raman spectra, including peak shifts, were analyzed to elucidate the distinctions between them. There are shifts in the Raman spectra of muscovites due to differences in pressure and temperature. The peak shifts, which typically develop in metamorphic rocks, occur due to the effects of temperature and, especially, pressure. In addition, it is known that peak shifts are also related to the content of elements such as Si and Al in muscovites. It is thought that metamorphic muscovites have undergone preferential orientation due to the pressure acting during metamorphism, and therefore, the peak intensity has increased, and the band width has increased due to structural defects arising from foliation developed as a result of the pressure during metamorphism. The results of this study demonstrate that the origin of muscovites and the rock types to which they belong can be identified by utilizing Raman spectra.

Keywords: Raman spectroscopy, Muscovite, S-type granites, Greenschist facies rocks.

Öz

Muskovit, levha silikatlar olarak da bilinen fillosilikatlara ait bir dioktahedral mika mineralidir. Beyaz mika olarak da adlandırılan muskovitler, magmatik, metamorfik ve sedimanter kayalar dahil olmak üzere tüm ana kaya gruplarında bulunabilir. Magmatik kayalarda özellikle S-tipi granitlerde ve pegmatitik kayalarda yaygın olan muskovitler, genellikle yeşilist fasiyesinde şist ve gnays bileşimindeki metamorfik kayalar içerisinde de değişen oranlarda yer almaktadır. Ana silikat türlerinden biri olan fillosilikatlar, değişken yapılar ve karmaşık kimyasal özelliklere sahiptirler. Bu yapısal ve bileşimsel farklılıklardan dolayı, fillosilikatların Raman kaymaları farklı spektral bölgelerde gözlemlenebilir. Bunun yanında, magmanın kristalleşme süreçlerindeki değişimler ve metamorfizma sırasındaki basınç-sıcaklık koşullarındaki farklılıklar, Raman spektrumlarının şiddetini ve dalga sayısını etkilemektedir. Bu çalışmada, magmatik ve metamorfik kökenli muskovitlerin Raman spektrumları karşılaştırılmış ve aralarındaki ayrımların ortaya konulabilmesi için pik kaymaları da dahil olmak üzere Raman spektrumlarındaki farklılıklar analiz edilmiştir. Basınç ve sıcaklık farklılıklarından dolayı muskovitlerin Raman spektrumlarında kaymalar bulunmaktadır. Genelde metamorfik kayalarda gelişen pik kaymaları, sıcaklık ve özellikle basıncın etkisiyle meydana gelmektedir. Bunun yanında pik kaymalarının muskovitlerdeki Si ve Al gibi bazı elementlerin içeriği ile de ilişkili olduğu bilinmektedir. Metamorfik muskovitlerin metamorfizma sırasında etkili olan basınç nedeniyle tercihli yönelime uğradığı ve bu nedenle pik şiddetinin arttığı, bant genişliğinin ise metamorfizma sırasındaki basınç sonucu gelişen foliasyondan kaynaklanan yapısal kusurlar nedeniyle arttığı düşünülmektedir. Bu çalışmanın sonuçları, Raman spektrumlarından yararlanılarak muskovitlerin kökeninin ve ait olduğu kaya türlerinin belirlenebileceğini göstermektedir.

Anahtar kelimeler: Raman spektroskopisi, Muskovit, S-tipi granitler, Yeşilist fasiyesi kayaları.

1 Introduction

Raman scattering was discovered in 1928 by the Indian physicist Chandrasekhara Venkata Raman (1888-1970). Raman spectroscopy, based on Raman scattering, provides essential information about the chemical structure of molecules. Since the vibrational energy level of each molecule is unique, the obtained Raman spectrum reveals the chemical fingerprint of the analyzed molecule. The masses of atoms, their

geometrical arrangements, and the strength of their chemical bonds determine the frequencies of molecular vibrations [1].

Raman spectroscopy is a practical, fast, and non-destructive spectroscopic method that can be used for qualitative and quantitative analysis of inorganic and organic samples [2]. Raman spectroscopy, which allows analyses on solid, liquid, and gaseous samples, has been successfully used in many different fields and disciplines. Raman spectroscopy also has an essential place in mineralogical determinations [3]-[12].

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Confocal Raman Spectroscopy (CRS) complements other spectroscopic methods, such as routine optical microscopy, chemical analysis, X-ray diffraction (XRD), and electron probe microanalysis (EPMA), in mineralogical and petrological investigations and even stands out as a powerful and advantageous alternative [13]-[18].

Various parameters, such as instrumental setup, structural defects, trace elements, internal stresses, and temperature and stress, can affect the Raman signal [8].

In this study, it is aimed to reveal the differences of muscovites in igneous and metamorphic rocks by comparing them according to Raman spectroscopic characteristics. Determining the effects of magmatic processes and metamorphic conditions on Raman spectra will provide a significant advantage in mineralogical determinations and genetic distinctions, and will support and complement routine optical microscopic examinations and other spectroscopic methods.

1.1 Structural compositional characteristics of micas

Phyllosilicates, which igneous, metamorphic, and sedimentary processes can form, have extremely complex structures and highly variable compositions. Phyllosilicates are divided into five different groups: kaolinite-serpentine group, pyrophyllite-talk group, mica group, smectite group, and chlorite group according to different types of T and Oc stacking sequences [19]. Here, T is used to represent tetrahedra filled by Si (and sometimes Al) as the central cation; Oc is used to represent octahedra with Mg, Fe²⁺, Fe³⁺, or Al as the central cation. The mica group of phyllosilicates has the structural-compositional feature of T-Oc-T-A (A=K, Na) [19]. The structural feature of muscovite [KAl₂(AlSi₃O₁₀)(OH)₂], a dioctahedral phyllosilicate, is the T-Oc-T-A stacking sequence in which A (normally Na⁺ or K⁺), sandwiched in the space between the T-Oc-T layers, represents the major cation [19]. In dioctahedral phyllosilicates, Al fills 2/3 of the Oc sites [20]. The crystal structure of muscovite consists of 2:1 layer or tetrahedral-octahedral-tetrahedral (TOT) layers connected by large interlayer cations. Within the tetrahedral sheet, individual tetrahedra are connected to neighboring tetrahedra through the sharing of their basal oxygens (bridging oxygen). The octahedral cation is coordinated by four apical oxygens (non-bridging oxygen) from the upper and lower tetrahedral sheets and two OH ions in the center of the six-fold rings formed by the apical oxygens [21].

1.2 Raman spectroscopic characteristics of micas

There are essential studies on the Raman spectroscopic characteristics of phyllosilicates and micas [15],[16],[19]-[29]. Raman spectra of phyllosilicates are generally located in four different spectral regions as i) 3800-3000 cm⁻¹, ii) 1150-800 cm⁻¹, iii) 800-600 cm⁻¹, and iv) <600 cm⁻¹. The Raman peaks observed in the spectral region between 3800-3000 cm⁻¹ are due to the stretching mode of OH or water in the structure of phyllosilicates [19],[20].

Tlili et al. [24] subdivided the Raman spectrum of micas into low wavenumber region (= 50-300 cm⁻¹), high wavenumber region (= 300-1250 cm⁻¹), and OH-stretching region (= 3500-3750 cm⁻¹) and investigated the differences in muscovite Raman spectra depending on whether the incident laser polarization is parallel or perpendicular to the plane of the slice.

McKeown et al. [26] calculated the Raman and IR-active modes of muscovites. They suggested that Raman modes at frequencies above 800 cm⁻¹ are composed primarily of internal tetrahedral sheet T-O stretching and T-O-T bending vibrations, modes between 800 and 360 cm⁻¹ have mixed internal tetrahedral sheet motions and K, and octahedral Al displacements, and modes at frequencies lower than 360 cm⁻¹ have lattice and OH motions.

According to Šontevska et al. [28], the high-frequency (about 1100 cm⁻¹) broad and complex band and the band around 900 cm⁻¹ in the Raman spectrum of muscovites represent Si-O-Si(Al) stretching vibrations, while the very weak band around 750 and 700 cm⁻¹ is likely due to O-Al-O bending vibrations. The lower frequency bands around 420 and 260 cm⁻¹ cannot be assigned to a single vibration type and are of mixed character, primarily linked to O-Al-O and O-Si-O translations, while the Raman peak at 190 cm⁻¹ can be assigned to Al-OH translational modes.

Singh and Singh [29] studied the vibrational spectroscopic properties of the layered phyllosilicates muscovite and biotite. They analyzed their Raman bands by comparing them with those of muscovites of different origins reported in the literature. According to the researchers, in the high-frequency region, the very strong band around 1127 cm⁻¹ and the moderate band around 914 cm⁻¹ correspond to Si-O-Si and Si-O-Al stretching vibrations, respectively. The moderate band around 755 cm⁻¹ and the strong band around 703 cm⁻¹ are due to O-Al-O bending vibrations. A very weak band is observed at 579 cm⁻¹ due to the bending property of Al-O-Al. The low-frequency strong bands around 407 cm⁻¹ and 263 cm⁻¹ are related to O-Al-O and O-Si-O translational modes. Due to Al-OH translations, a moderate Raman peak is observed around 197 cm⁻¹.

Li et al. [21] investigated the correlation between Raman spectra and mineral compositions of natural muscovites and phengites. They revealed the Raman characteristics of these minerals across varying Si content and observed peak splitting, peak disappearance, and changes in peak intensity in the Raman spectra with increasing Si content.

Akçe and Kadioğlu [15] examined the Raman characteristics of white micas within S-type granites. Their analysis of muscovite spectra indicated distinct bands: Si-O-Si(Al) stretching vibrations observed between 1200 and 875 cm⁻¹; O-Al-O bending vibrations identified in the 750-650 cm⁻¹ range; bands of mixed-character primarily related to O-Al-O and O-Si-O translations between 500 and 225 cm⁻¹; Al-OH and sheet translations occurring between 225 and 75 cm⁻¹; and finally, stretching vibrations of O-H or C-H groups recorded within the 2800-3623 cm⁻¹ region.

Deniz [16] studied mica types as indicators of magma origin and used Confocal Raman Spectroscopy (CRS), Fourier Transform Infrared (FTIR) Spectroscopy and Confocal Raman Spectroscopy to determine the origin of giant micas at the boundary of syenites and metamorphic basement in Central Anatolia and the processes causing their formation, X-Ray Diffractometer (XRD), Polarized Energy Dispersive X-Ray Fluorescence Spectrometer (PED-XRF) and Electron Probe Micro Analysis (EPMA) were used for mineralogical, petrographic and geochemical analyses and spectroscopic characterization. The researcher compared the Raman spectra of different micas in the study area and revealed the changes in

Raman modes. Muscovite is recognized as one of the most important guide minerals in both igneous and metamorphic rocks. Muscovite can be formed from the partial melting of igneous or any other type of rock. In addition, it represents the main mineral composition in S-type granites. It is also the main mineral in pegmatitic and other igneous rocks, represented mainly by sericite, a mineral formed by decomposition. It is observed that feldspars in these rocks are transformed into small muscovite flakes (sericite) as a result of decomposition under the influence of hydrothermal solutions or atmospheric conditions.

Muscovite is also an essential mineral in metamorphic rocks and has indicator mineral properties. It is one of the indicator minerals that can represent a metamorphic belt and is generally the main component of metamorphic rocks, particularly mica schists and gneisses, in the greenschist facies. Muscovite is distinguished petrographically under the microscope due to its texture characteristics in igneous and metamorphic rocks. Since muscovites are formed under different temperature and pressure conditions, there should be a difference between molecular bond vibrations/exchanges. Therefore, this study was designed to distinguish muscovites in igneous and metamorphic rocks based on their Raman characteristics.

In this investigation, Raman characteristics of muscovites in S-type granites and muscovites formed in greenschist facies rocks were utilized to determine the behavioural changes in Raman spectra. We mainly tried to determine rock types by using the Raman spectral differences between muscovite in igneous and metamorphic rocks. As a result of this study, an attempt was made to identify and differentiate rocks formed by igneous partial melting and rocks in metamorphic greenschist facies formed under low temperature-low pressure conditions using the Raman characteristic spectra of muscovites.

2 Material and methods

This study was carried out in four stages: literature review, field studies, laboratory studies, and office studies.

Field studies were carried out in the S-type leucogranites containing muscovite in the northern part of the Yozgat Intrusive Complex (YIC) and in the Kırşehir metamorphites (KM) [30] with quartz micaschist composition in the southern part of the Kırşehir Massif, and rock samples were taken for the study.

Within the scope of the laboratory studies, the thin sections were prepared from rock samples collected during the field

studies. Then, thin sections were examined under a Zeiss Axio model polarising microscope to determine the mineralogical composition and petrographic properties of the rocks.

Based on the petrographic determination, the Raman spectroscopic characteristics of muscovites selected from samples of igneous and metamorphic rocks were analyzed. The CRS analysis was performed using a high-resolution Thermo Scientific DXR model confocal Raman spectrometer in Ankara University YEBİM laboratories. The selected muscovites on polished thin sections were marked under a polarizing microscope. Then Raman spectroscopic measurements were performed by laser excitation at a wavelength of 633 nm with a slit aperture of 25 μm and 600 lines/mm grating (estimated resolution: 2.6-4.4 cm^{-1} and estimated spot size: 0.7 μm). As a result of CRS measurements, spectra of muscovites in the Raman shift range of 50-3623 cm^{-1} were obtained.

The data obtained as a result of the literature review, field, and laboratory studies were evaluated together, and the Raman spectroscopic criteria that enable the differentiation of muscovites in igneous and metamorphic rocks were tried to be determined in this study.

3 Results and discussion

3.1 Petrography

The scope of this study: S-type granites distributed in the vicinity of Sarıhacılı in the northern part of the YIC and KM rocks with quartz mica schist composition observed in the vicinity of Kırşehir province in the southern part of the Kırşehir Massif were examined.

The granitoids distributed in and around Sarıhacılı village in the northern part of YIC are generally light pink-coloured, leucocratic S-type granites rich in felsic components [31]-[33]. These rocks, which have an alkali feldspar granite composition, are composed of approximately equal-sized components and, macroscopically, exhibit a phaneritic, sometimes porphyrophaneritic texture with occasional coarse quartz (Figure 1a). Examined under a polarising microscope, these granites are mainly composed of quartz, alkali feldspar, biotite, muscovite, and plagioclase minerals and have holocrystalline hypidiomorphic texture (Figure 1b, c). The muscovites, which are the subject of this study, are characterized by their white colour in the hand specimen, their generally slab-like, colourless, low relief and parallel extinction in thin section examinations, and their high interference colours.



Figure 1. Macroscopic and microscopic images of Sarıhacılı S-type granites.
(a): Field photograph. (b): Photomicrograph (Parallel Nicol). (c): Photomicrograph (Crossed Nicol).

KM, which are typically located in the vicinity of Kuşdilli village of Kırşehir Province in the southern part of Kırşehir Massif, have a foliated texture and quartz mica schist composition (Figure 2a). They are mainly composed of muscovite, biotite, and feldspar minerals, rich in quartz, and have a lepidogranoblastic texture under the microscope (Figure 2b, c).

3.2 Confocal Raman spectroscopy

Within the scope of confocal Raman spectroscopy investigations, CRS point measurements of igneous muscovites in S-type granites and metamorphic muscovites in quartz mica schists were made, spectra in the 50-3623 cm^{-1} wave number range were obtained, and these spectra were scanned with Spectral ID software and matched with reference mineral spectra and it was determined that they have muscovite in composition. Raman images of the muscovites, whose spectra were analysed in the wavenumber ranges 50-1250 cm^{-1} and 3000-3623 cm^{-1} , were also obtained, and it was observed that they generally had clean surfaces and exhibited strong Raman bands consistent with the reference spectra (Figure 3). However, when the Raman spectra were analysed in detail, significant differences were observed between igneous and metamorphic muscovites. The Raman spectral differences between these muscovites are explained, and their band characteristics are compared with experimental results reported in previous studies (Table 1 and Figure 3). The Raman spectroscopic data from Akçe and Kadioğlu [15] were significantly utilized during the examination of the Raman spectra of igneous muscovites in S-type granites. The Raman characteristics of muscovites are shifts in the Raman spectra due to pressure and temperature differences; certain peaks are observed more prominently. The shifting structures of the peaks occur mostly in metamorphic rocks due to the effects of pressure and temperature, especially pressure, and significant shifts in the Raman peaks of muscovite were detected under regional metamorphic conditions. The spectral data, spectral regions with significant Raman shift values reveal that the strong Raman peaks of igneous muscovites are observed at 3623, 698, 258, and 97 cm^{-1} ; moderate Raman peaks at 417 and 188 cm^{-1} ; weak Raman peaks at 1185, 1111, 966, 915, 836, 786, 744, 637 and 540 cm^{-1} . Strong Raman peaks of metamorphic muscovites are observed at 709, 272, 206, and 110 cm^{-1} ; moderate Raman peaks at 3621, 1069, 758, and 418 cm^{-1} ; the weak Raman peaks at 1118, 918, 826, 648, 549, and 492 cm^{-1} . Taking advantage of previous studies ([19],[20],[22],[24],[26],

[28],[29]), the Raman modes of muscovites were assigned. Within the spectral range between 3623-3000 cm^{-1} , bands are arising from OH or structural H_2O stretching vibrations. Raman peaks in the 1200-780 cm^{-1} spectral region are due to tetrahedral (SiO_4 tetrahedra) vibrations. The bands in the high frequency region in the range of 1150-1040 cm^{-1} are attributed to T- O_{br} stretching, while the bands in the range of 1040-870 cm^{-1} are attributed to T- O_{nb} stretching motions. The bands in the 850-780 cm^{-1} range are associated with the T- O_{br} -T bending motion. The bands in the range 780-660 cm^{-1} belong to O-Al-O bending vibrations. The band in the range 660-630 cm^{-1} is assigned to the translational motions of O_{br} and O_{nb} . The band in the range 600-510 cm^{-1} is due to tetrahedral vibrations and belongs to Al-O-Al bending. The band in the range 510-470 cm^{-1} is associated with K z- translation + tetrahedral rotation || z + M2- O_{nb} stretching motions, where tetrahedral rotations are mixed with M2-O stretching according to McKeown et al. [26]. Over the spectral interval of 470-230 cm^{-1} , there are low frequency bands associated with O-Al-O and O-Si-O translations. In the low-frequency spectral region between 230 and 75 cm^{-1} , bands related to Al-OH and sheet translations are observed (Figure 3).

The Raman spectra of igneous and metamorphic muscovites were compared and analysed in detail. OH stress vibrations are represented by a strong band at 3622.65 cm^{-1} in igneous muscovites and a strong and broad band at 3621.33 cm^{-1} in metamorphic muscovites in accordance with the band characteristic for muscovite micas in the literature. Si-O-Si stretching vibrations in the high frequency region are represented by a single weak, broad, and asymmetric band at 1110.62 cm^{-1} in igneous muscovites. In contrast, in metamorphic muscovites, they are represented by a very weak band at 1117.99 cm^{-1} and a broad band of moderate intensity at 1068.74 cm^{-1} . Si-O-Al stretching vibrations are represented by two very weak bands at 915.22 and 965.80 cm^{-1} in igneous muscovites and a single very weak band at 917.55 cm^{-1} in metamorphic muscovites. T- O_{br} -T bending motion is represented by a very weak band at 835.98 cm^{-1} and a weak band at 785.94 cm^{-1} in igneous muscovites and a single very weak band at 825.66 cm^{-1} in metamorphic muscovites. O-Al-O bending vibrations are represented by a weakly intense band at 744.21 cm^{-1} and a strong band at 698.18 cm^{-1} in igneous muscovites and by a moderately intense band at 757.73 cm^{-1} and a strong band at 709.35 cm^{-1} in metamorphic muscovites.

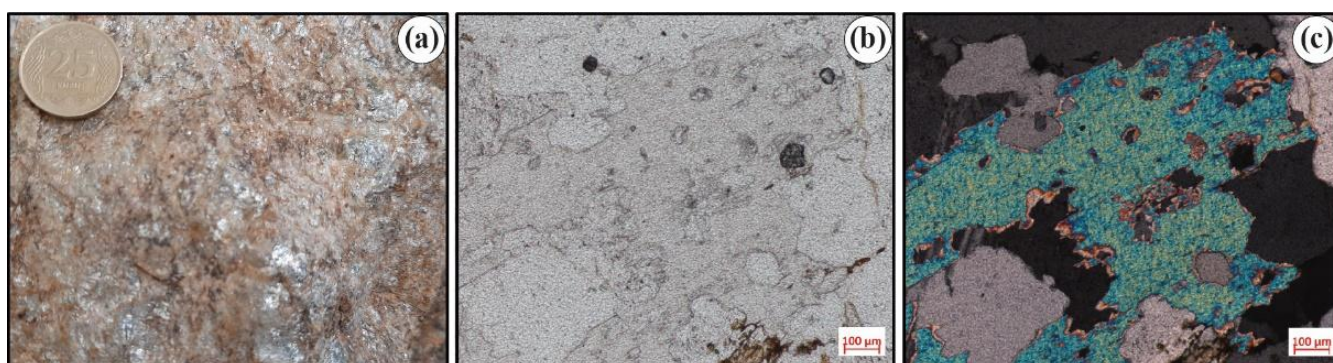


Figure 2. Macroscopic and microscopic images of quartz mica schists in the vicinity of Kırşehir-Kuşdilli. (a): Field photograph. (b): Photomicrograph (Parallel Nicol). (c): Photomicrograph (Crossed Nicol)).

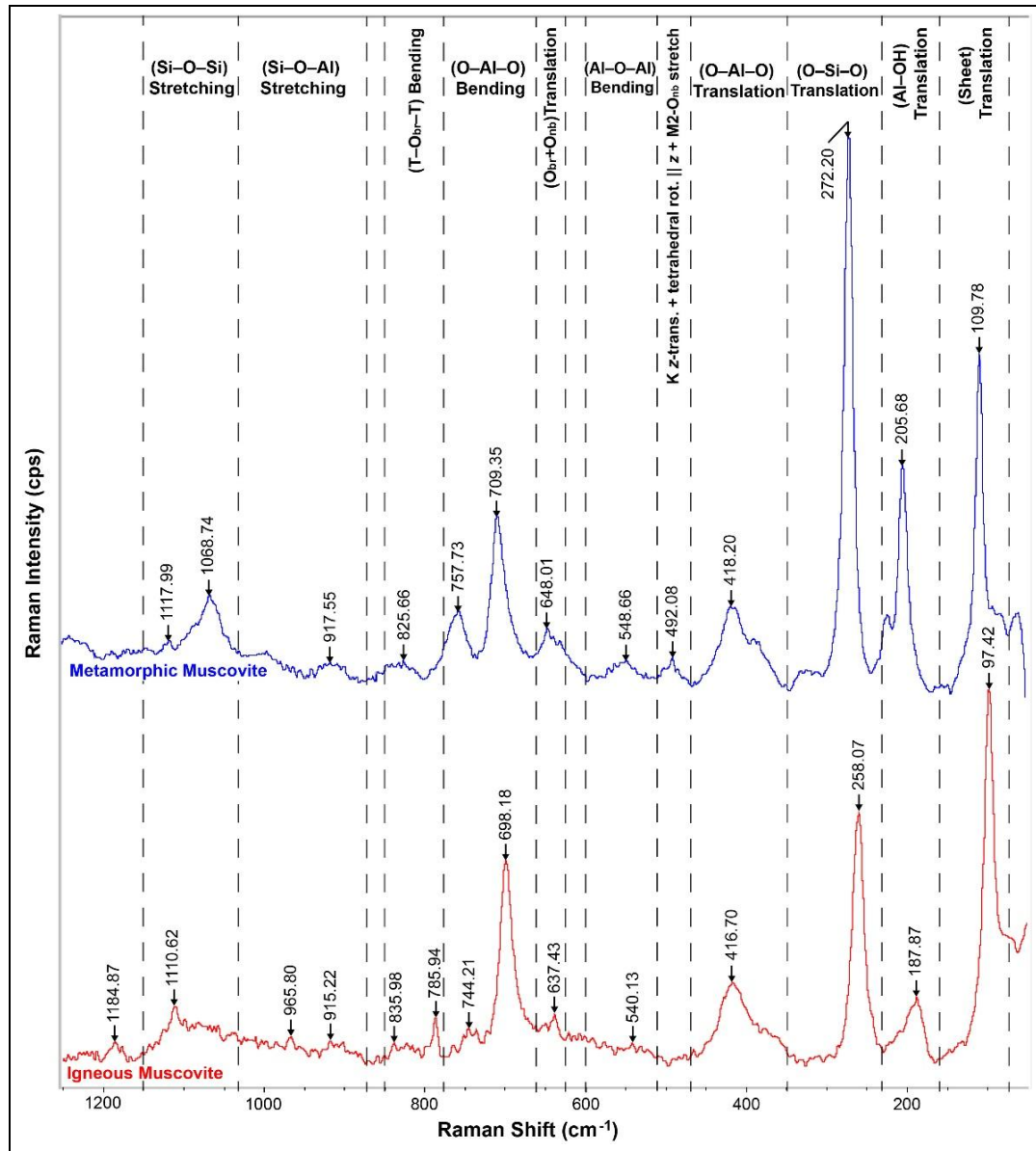


Figure 3. Results of the Confocal Raman spectra of igneous muscovite and metamorphic muscovites.

Table 1. Mode assignments of the bands in the Raman spectra of muscovites investigated by different researchers.

Assignment	McKeown et al. [26]	Šontevska et al. [28] (Dunje)	Šontevska et al. [28] (Nežilovo)	Singh and Singh [29] (Nilore)	Akçe and Kadioğlu [15] (Igneous muscovite)	This study (Metamorphic muscovite)
v(OH)	-	-	-	-	3623 (s)	3621 (m,br)
v(Si-O-Si)	1116 (m)	1097 (vw,br)	1097 (w)	1127 (vs)	1111 (w,br)	1118 (vw)
v(Si-O-Si)	1098 (w)	-	-	-	-	1069 (m,br)
v(Si-O-Al)	912 (w)	900 (vw)	902 (vw)	914 (m)	915 (vw)	918 (vw)
δ(O-Al-O)	754 (s)	752 (vw)	751 (vw)	755 (m)	744 (w)	758 (m,br)
δ(O-Al-O)	704 (s)	703 (s)	701 (s)	703 (s)	698 (s)	709 (s)
δ(Al-O-Al)	542 (w)	-	-	579 (vw)	540 (vw)	549 (vw)
δ(O-Al-O)	410 (s)	419 (m,br)	420 (m)	407 (s)	417 (m,br)	418 (m,br)
δ(O-Si-O)	265 (vs)	262 (vs)	262 (s)	263 (vs)	258 (vs)	272 (vs)
L(Al-OH)	199 (m)	191 (m)	188 (w)	197 (m)	188 (m)	206 (s)
Sheet translation	101 (m)	-	-	-	97 (vs)	110 (vs)

* s: strong; m: medium; w: weak; v: very; br: broad (Raman shifts in cm⁻¹).

The weak band at 637.43 cm⁻¹ in igneous muscovites and the weak band at 648.01 cm⁻¹ in metamorphic muscovites belong to the translational motions of O_{br} and O_{nb}. Al-O-Al bending vibrations are represented by a very weak band at 540.13 cm⁻¹ in igneous muscovites and a weak band at 548.66 cm⁻¹ in metamorphic muscovites. The band of mixed character, in which tetrahedral rotations are mixed with M2-O stretching, is represented by a weakly intense band at 492.08 cm⁻¹ in metamorphic muscovites, but this band is absent in the spectrum of igneous muscovites. O-Al-O translations are represented by a moderately strong and broad band at 416.70 cm⁻¹ in igneous muscovites and a moderately strong and broad band at 418.20 cm⁻¹ in metamorphic muscovites.

O-Si-O translations are represented by very strong bands at 258.07 cm⁻¹ in igneous muscovites and 272.20 cm⁻¹ in metamorphic muscovites. Al-OH translations are represented by a moderate band at 187.87 cm⁻¹ in igneous muscovites and a strong band at 205.68 cm⁻¹ in metamorphic muscovites. Peaks arising from sheet translations and representing the spectrally lowest frequency bands are found as very strong bands at 97.42 cm⁻¹ in igneous muscovites and 109.78 cm⁻¹ in metamorphic muscovites (Table 1 and Figure 3).

The bands of OH stretch vibrations around 3621-3623 cm⁻¹ are compared, it is seen that the peak of metamorphic muscovites and the peak of igneous muscovites have close wavenumber and intensity, but the peak of metamorphic muscovites is wider than that of igneous muscovites. The increase in bandwidth is mainly due to structural defects in the mineral. Here, the fact that metamorphic muscovites have a foliated (schistosity) texture due to the pressure effective during metamorphism and the resulting structural defects may be the reason for the high bandwidth.

The Si-O-Si stretching vibration bands within the 1150-1040 cm⁻¹ range are compared. It is seen that the peak around 1111 cm⁻¹ in igneous muscovites shifts to around 1118 cm⁻¹ in metamorphic muscovites, and the intensity of the peak is very weakened. The peak shift is mainly due to changes in chemical bond lengths resulting from exposure of the mineral to temperature and/or stress.

The peak shift in metamorphic muscovites here may have occurred due to the temperature and especially the pressure effective during metamorphism. The Si-O-Si stretching vibration peak around 1069 cm⁻¹ is observed only in metamorphic muscovites, not in igneous muscovites.

Comparing the Si-O-Al stretching vibration bands around 915-918 cm⁻¹, it is observed that the weak peak at approximately 915 cm⁻¹ in igneous muscovites is slightly shifted to around 918 cm⁻¹ in metamorphic muscovites, likely due to the effects of temperature and pressure during metamorphism. Additionally, a weak band around 966 cm⁻¹, also corresponding to Si-O-Al stretching vibrations, is present in igneous muscovites but absent in metamorphic muscovites.

When the band associated with the T-O_{br}-T bending motion around 826-836 cm⁻¹ is compared, it appears that the weak peak at approximately 836 cm⁻¹ in igneous muscovites may have shifted to around 826 cm⁻¹ in metamorphic muscovites, likely due to the effects of temperature and pressure during metamorphism. Additionally, the band corresponding to the T-O_{br}-T bending motion around 786 cm⁻¹ is observed only in igneous muscovites and is absent in metamorphic muscovites.

When analyzing the band associated with O-Al-O bending vibrations in the range of 744-758 cm⁻¹, it is suggested that the peak around 744 cm⁻¹ in igneous muscovites may have shifted to approximately 758 cm⁻¹ in metamorphic muscovites due to the temperature and pressure conditions experienced during metamorphism. Additionally, it is proposed that metamorphic muscovites may have undergone preferential orientation due to metamorphic pressure, leading to an increase in peak intensity. Similarly, for the band corresponding to O-Al-O bending vibrations in the 698-709 cm⁻¹ range, the peak near 698 cm⁻¹ in igneous muscovites may have shifted to around 709 cm⁻¹ in metamorphic muscovites due to temperature and pressure, with a slight decrease in peak intensity attributed to preferential orientation.

Concerning the band related to the translation motions of O_{br} + O_{nb} in the 637-648 cm⁻¹ range, it is believed that the peak near 637 cm⁻¹ in igneous muscovites may have shifted to around 648 cm⁻¹ in metamorphic muscovites due to the temperature and pressure conditions during metamorphism. Additionally, the band width is thought to have increased due to structural defects induced by foliation from metamorphic pressure. According to the literature, this shift from around 637 cm⁻¹ to approximately 648 cm⁻¹ may also be linked to an increase in wavenumber that is directly proportional to the rising Si⁴⁺ content [21].

Analyzing the band corresponding to Al-O-Al bending vibrations around 540-549 cm⁻¹, it is hypothesized that the weak peak at approximately 540 cm⁻¹ in igneous muscovites may have shifted to around 549 cm⁻¹ in metamorphic muscovites due to the prevailing temperature and pressure conditions during metamorphism, with an increase in peak intensity due to preferential orientation.

For the band related to O-Al-O translations around 417-418 cm⁻¹, the peak in metamorphic muscovites appears to have undergone a very slight shift compared to igneous muscovites, likely caused by the temperature and pressure conditions during metamorphism. Previous studies indicate that this shift is closely related to the elemental composition of white micas, showing a positive correlation between the Raman shift value and the Si, Fe, and Mg content, and a negative correlation with the Al, K, and Na content [21],[34],[35]. Accordingly, it can be inferred that the content of Si, Fe, and Mg in metamorphic muscovites may have increased relative to igneous muscovites, while the Al, K, and Na content may have decreased.

Considering the band corresponding to O-Si-O translations around 258-272 cm⁻¹, the peak at approximately 258 cm⁻¹ in igneous muscovites is thought to have shifted to around 272 cm⁻¹ in metamorphic muscovites, primarily due to the influence of temperature and especially pressure during metamorphism. This pressure may also have led to a preferential orientation in metamorphic muscovites, potentially increasing peak intensity.

For the band associated with Al-OH translations around 188-206 cm⁻¹, it is proposed that the peak at around 188 cm⁻¹ in igneous muscovites may have shifted to approximately 206 cm⁻¹ in metamorphic muscovites due to the temperature and particularly the pressure during the metamorphic process. The increased pressure may have caused the muscovites to exhibit preferential orientation, thereby increasing peak intensity. Additionally, a shoulder peak may have emerged in the metamorphic muscovite band due to structural defects

associated with foliation under metamorphic pressure. Previous studies suggest a possible relationship between this peak shift and the Si and Al content of muscovites [21],[24],[34]. Thus, the observation of the same peak around 188 cm⁻¹ in igneous muscovites at approximately 206 cm⁻¹ in metamorphic muscovites may be attributed to lower Si content and higher Al content in metamorphic muscovites compared to igneous muscovites.

Finally, for the band resulting from layer translations around 97-110 cm⁻¹, it is believed that the peak at approximately 97 cm⁻¹ in igneous muscovites may have shifted to around 110 cm⁻¹ in metamorphic muscovites, primarily due to the temperature and especially the pressure conditions during metamorphism.

4 Conclusions

Muscovite is considered one of the most indicator minerals in both igneous and metamorphic rocks. It is a significant mineral that can form from the partial melting of any rock type, whether igneous, metamorphic, or sedimentary. For this reason, muscovite is found as a primary mineral in S-type granites. Muscovites can also be found as a primary mineral in pegmatitic rocks. Still, in other igneous rocks, they are usually part of the sericite composition formed by the alteration of feldspars.

Muscovite is also an important mineral in metamorphic rocks and is one of the index minerals that represent a metamorphic zone. In metamorphic rocks, muscovite is generally a major component of mica schists and gneisses within the greenschist facies.

Igneous and metamorphic muscovites can be distinguished petrographically under a microscope due to their different textural characteristics. Muscovites derived from various sources and thus form under different temperature and pressure conditions, there are some differences in their molecular bond vibrations. When examining the Raman spectra of muscovites, distinct shifts are observed in the Raman peaks of metamorphic muscovites due to the effects of pressure and temperature from regional metamorphism; some peaks become more pronounced, while others may disappear.

In this study, the Raman spectroscopic characteristics of muscovites formed under igneous conditions in S-type granites were compared with those of muscovites formed in the greenschist facies under regional metamorphic conditions, and changes in the behaviour of the Raman spectra were identified. The shifts and intensity changes in the Raman values of modes representing the same vibrations of igneous and metamorphic muscovites were examined in detail, the reasons for these changes were explained, and it was demonstrated that these muscovites of different origins can be distinguished from each other from a confocal Raman spectroscopic perspective.

The results of this study revealed that the origin and the rock types to which muscovites belong can be identified by utilizing the differences in the characteristic Raman spectra of igneous and metamorphic muscovites. Thus, by examining the Raman spectra, it can be determined whether the muscovites belong to igneous rocks formed by partial melting or to metamorphic rocks formed in the greenschist facies, which characterizes low temperature and low-pressure conditions. Perhaps the most important aspect of this study is that it is possible to determine whether muscovites are igneous or metamorphic based solely

on Raman spectroscopic studies. Therefore, if igneous muscovites are identified, it may indicate partial melting due to the crustal compression in the region; if metamorphic muscovites are identified, it may indicate the development of an orogenic metamorphism related to the formation of orogenic belts and ore deposits. Hence, examining muscovites with Raman spectroscopy can potentially enable the identification of these belts.

Because of their similar behaviour, S-type granites and I-type granites can sometimes be confused with each other. This study will also help distinguish S-type granites, and it will allow to determine the origin and source of granites by using the Raman spectrum properties of muscovites in the granites.

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6 Author contribution statements

In the study carried out, Musa Avni Akçe contributed to the formation and design of the idea, literature review, field observations and sample collection, petrographic examinations, CRS analyses, evaluation of the data obtained, and writing of the manuscript; Yusuf Kağan Kadioğlu contributed to the formation and design of the idea, petrographic examinations, CRS analyses, evaluation and interpretation of the results, spell checking, and review of the manuscript for content.

7 Ethics committee approval and conflict of interest statement

"There is no need to obtain permission from the ethics committee for the article prepared". "There is no conflict of interest with any person/institution in the article prepared".

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