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RAMAN SPECTROSCOPIC CHARACTERISTICS OF MELANITE BEARING FOID SYENITES: YOZGAT INTRUSIVE COMPLEX

MELANİT İÇEREN FOİD SİYENİTLERİN RAMAN SPEKTROSKOPİK KARAKTERİSTİKLERİ: YOZGAT İNTRÜZİF KOMPLEKSİ

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ABSTRACT

The foid bearing syenites within the Yozgat Intrusive Complex (YIC), have coarse crystalline, euhedral, dark-black coloured in hand specimen melanite type garnet. They are mainly crop out in Sivritepe, Gedikhasanlı, Mükremin, Karlı hills and Çağlayan vicinity. Foid bearing syenites generally are in the composition of pyroxene syenite, foid syenite, melanite bearing foid syenite, foid syenite porphyry and pyroxene bearing foid syenite porphyry. The scope of this study, is to use the Raman spectra of melanites of the foid syenites to evaluate their significant behavior in the crystallization process of the unit. Melanites are represent the member of the black andradite type of the garnet group. Melanite, is crystallized from the silica undersaturated magma with the $Ca_3(Fe^{3+},Ti)_2(SiO_4)_3$ chemical formula. Melanites exhibit clear with high spectrum in Raman spectroscopic determinations due to the silicate structure form and their high symmetrical habit within the crystal systems. The melanites are dark brown in color, euhedral shape, with high optical relief and are isotropic under the polarizing microscope. Raman spectra of melanites are identical with the andradite in composition and generally show Raman shift peaks in the range of 170-1000 cm^{-1}. The melanite has 13 spectra in the total, of the 12 spectra of these spectra are asymmetrical and only one spectra has symmetrical character. Three groups of Raman spectra of the melanite-type are identical with the andradites Raman spectra. These are distributed as 371 cm^{-1}, 522 cm^{-1} and 879 cm^{-1} respectively. The Raman spectra of the melanites are obtained in two main regions: (a) external vibration below 400 cm^{-1} and (b) internal vibration above 400 cm^{-1}. The first part of the external vibration up to 400 cm^{-1} is related to SiO_4 tetrahedra and divalent cations. The internal vibration of these garnets belongs to the SiO_4 and their spectra are wavenumber ranges of 400-1050 cm^{-1}. Si-O bending modes are observed in the spectral region between 400 and 600 cm^{-1}, and Si-O stretching modes are observed in the spectral region between 700 and 1050 cm^{-1}. The compositional spectra and vibrational modes of the melanites in the YIC show that the crystallization and differentiation processes have been affected by the interaction of different sources of the components rather than the pure main silica undersaturated magma during their crystallization.

Keywords: Yozgat Intrusive Complex, Melanite, Confocal Raman Spectroscopy

ÖZET

Yozgat İntrüzif Kompleksi (YİK)'nde foid içeren siyenitler iri kristalize, özşekilli, el örneğinde koyu-siyah renkli melanit bileşimli granatlar içermektedir. Bunlar daha çok Sivritepe, Gedikhasanlı, Mükremin, Karlı tepeleri ve Çağlayan civarlarında tipik olarak yüzeylenmektedir. Foid içeren siyenitler genel olarak siyenit, foid siyenit, melanitli foid siyenit, foid siyenit porfir, piroksenli foid siyenit porfir bileşimlerine sahiptirler. Bu çalışma kapsamında YİK'nin doğu bölümündeki foid siyenitler içerisindeki melanitlerin Raman spektraları incelenerek kristalizasyon sürecindeki önemleri ortaya konulmuştur. Melanitler, siyah renkli andradit türü granat grubuna girmektedir. Genel olarak $Ca_3(Fe^{3+},Ti)_2(SiO_4)_3$ kimyasal bileşimini sergileyen melanit, silikaca doygun olmayan alkali magmatik kayalar içerisinde tipik olarak görülebilmektedir. Melanitler, Raman spektroskopik incelemelerinde silikat yapısı formu ve kristal sistemlerindeki yüksek simetriden dolayı belirgin ve yüksek spektrum sergilerler. Siyenitler içerisindeki melanitler polarizan mikroskop altında incelendiğinde koyu kahve renkli, özşekilli, yüksek optik engebeye sahip ve izotropturlar. Melanitlerin Raman spektraları andradit bileşimli olup genel olarak 170-1000 cm^{-1} aralığında Raman kayma pikleri göstermektedir. Toplamda 13 spektrum gösteren bu granatların 12 spektrumu asimetrik bir spektrumu ise simetriktir. Melanit türü andraditlerde 3 grup Raman spektrası izlenmiştir. Bunlar sırasıyla 371 cm^{-1}, 522 cm^{-1} ve 879 cm^{-1} Raman kayma spektrumlarıdır. Melanitlerin Raman spektrası (a) dış titreşimi 400 cm^{-1}'in altında ve (b) iç titreşimi ise 400 cm^{-1}'in üstünde olanlar şeklinde başlıca iki bölgede elde edilmiştir. Dış titreşimin 400 cm^{-1}'e kadar olan ilk kısmı SiO_4 tetrahedrası ve iki değerlikli katyonlarla ilişkilidir. Bu granatların iç titreşimi Si-O bağlarına ait olup spektrumları 400-1050 cm^{-1} dalga sayısı aralığındadır. Si-O bükülme modları 400 ile 600 cm^{-1} arasındaki, Si-O gerilme modları ise 700 ile 1050 cm^{-1} arasındaki spektral bölgede görülmektedir. YİK'ndeki melanitlerin bileşimsel spektrumları ve titreşimsel modları, kristalleşmeleri sırasında kristalizasyon ve diferansiyon süreçlerinin silikaca doygun olmayan saf ana magmadan ziyade bileşenlerin farklı kaynaklarının etkileşiminden etkilendiğini göstermektedir.

Anahtar Kelimeler: Yozgat İntrüzif Kompleksi, Melanit, Konfokal Raman Spektroskopisi

INTRODUCTION

Yozgat Intrusive Complex (YIC) is the largest intrusive body in terms of distribution in the Central Anatolian Crystalline Complex (CACC), and consists of granitic, gabbroic, monzonitic and syenitic rocks with different composition and character. This intrusive rock assemblage, which was called as "Yozgat Batholith" and "Composite Yozgat Batholith" in previous studies (Boztuğ, 1994, Tatar and Boztuğ, 1998), was first defined and named as "Yozgat Intrusive Complex" by Akçe and Kadıoğlu (2009).

Akçe and Kadıoğlu (2009) and Akçe (2010) made a detailed differentiation map of the Yozgat Intrusive Complex, examined the geological, petrological, Raman spectroscopic and mineral chemistry characteristics, and made the Ar-Ar age determination and geodynamic evolution modeling in the light of all these data. Thus, they contributed to the interpretation of the magmatism that developed in the Cretaceous period of Central Anatolia. The YIC syenitic rocks, most typically observed around Sivritepe, were named as "foid-bearing Sivritepe syenitoids" (Akçe, 2010).

Melanite is black in color and is the member of an andradite variety garnet group mineral. Melanite is a nesosilicate and sometimes referred to as "titanian andradite". Melanite typically crystallizes from the silica unsaturated magma. Melanites, like other garnets, exhibit strong

Raman peaks due to their silicate structure and high symmetry in their crystal systems. The aim of this study is to reveal the Raman spectroscopic characteristics of melanite bearing foid syenites within the Yozgat Intrusive Complex.

In terms of regional geology, the study area is located within the Kırşehir Massif, which is represents one of the main tectonic units of Turkey. The study area comprises the eastern part of the Yozgat Intrusive Complex located in the northern part of the Central Anatolian Crystalline Complex (Figure 1).

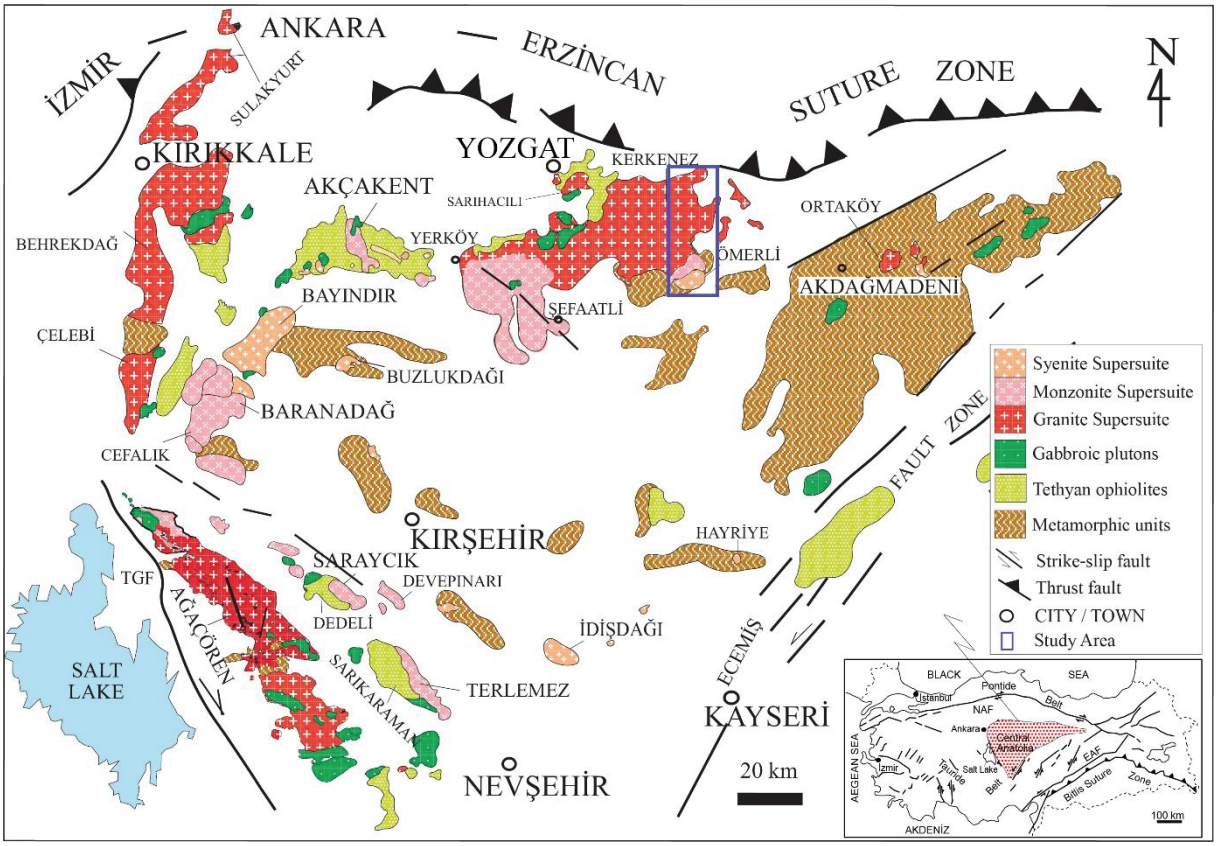

Figure 1. Simplified geological map of the Central Anatolian Crystalline Complex (modified from Kadıoğlu et. al, 2006).

MATERIALS AND METHODS

This research consists of literature review, geological fieldwork, laboratory study and evaluation of all data obtained.

Geological fieldworks were carried out in the melanite-bearing foid syenites located in the eastern part of the Yozgat Intrusive Complex. As a result of the fieldwork, polished thin sections were prepared from the rock samples collected, and as a result of detailed mineralogical and petrographic examinations, their mineralogical compositions and microscopic textural properties were revealed. Petrographic examinations were made using a Leica DMLP model polarizing microscope.

Raman spectroscopic characteristics of melanites selected from rock samples representing foid syenites as a result of petrographic examination were investigated. Confocal Raman spectroscopy examination was performed using a high-resolution Thermo Scientific DXR model confocal Raman spectrometer. Raman spectroscopic measurements of the melanites,

whose locations were determined and marked on polished thin sections, were performed by laser excitation at a wavelength of 633 nm in a Raman spectrometer with a slit aperture of 25 μm and a grating value of 600 lines/mm (estimated resolution: 2.6-4.4 cm^{-1} and estimated spot size: 0.7 μm), and their spectra in the wavenumber range of 200-1250 cm^{-1} were obtained.

RESULTS AND DISCUSSION

Geology and Petrography

The syenitic rocks, which are the subject of the study, are located in the eastern part of the Yozgat Intrusive Complex and outcrop as independent bodies along a line between Gedikhasanlı in the south and Mükremin villages in the north.

The syenitic rocks within the Yozgat Intrusive Complex are in the composition of pyroxene syenite, foid syenite, melanite bearing foid syenite, foid syenite porphyry and pyroxene bearing foid syenite porphyry. These syenitic rocks are mainly crop out in Sivritepe, Gedikhasanlı, Mükremin, Karlı hills and Çağlayan vicinity and cut both the Gavurdağı and Kerkenez granitoid units around Çağlayan village (Akçe, 2010).

The foid syenites within the Yozgat Intrusive Complex contain coarse crystalline, euhedral and black colored in hand specimen melanite type garnets. These syenitic rocks in the study area are generally pinkish, pinkish gray and pinkish green in color, contain large nephelines in places and exhibit phaneritic and porphyro-phaneritic textures (Figure 2).

Foid syenite and foid syenite porphyries examined under polarizing microscope are composed of coarse orthoclase, nepheline, pyroxene and melanite composition and exhibit hypidiomorph porphyric texture. The examined melanites are dark brown in color, euhedral, subhedral and anhedral, high optical relief and isotropic under the microscope (Figure 2).

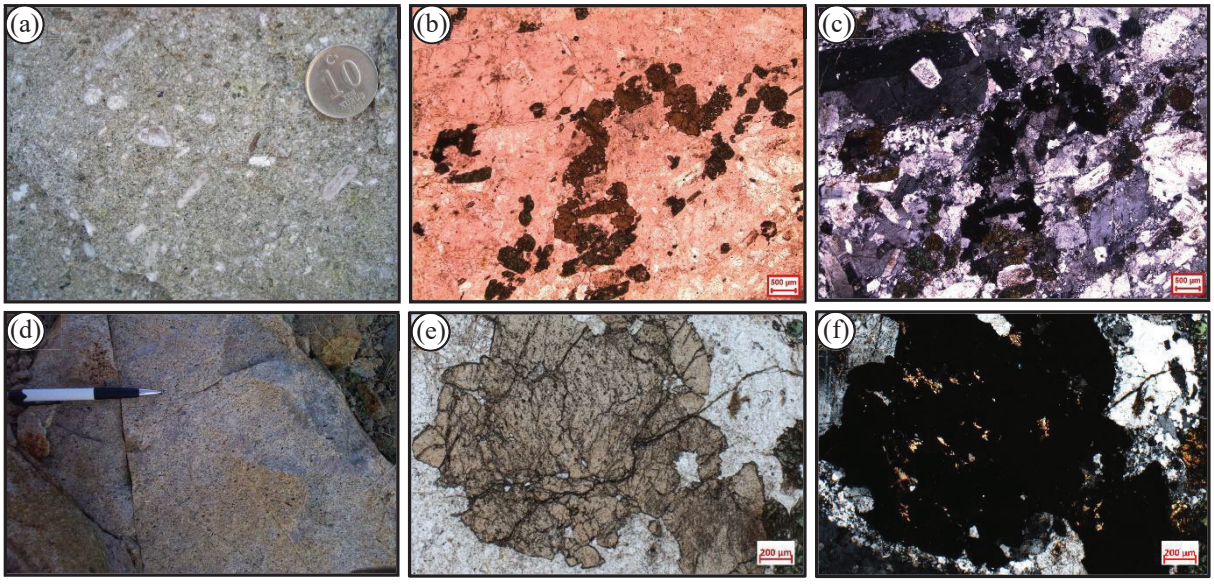

Figure 2. (a) and (d): Macroscopic aspects of foid syenites in the eastern part of YIC (b), (c), (e) and (f): Photomicrographs of foid syenites in the eastern part of YIC ((b), (e): Crossed Nicol; (c), (f): Parallel Nicol)

Confocal Raman Spectroscopy

Within the scope of this study, the Raman spectra of the melanites in the foid syenites in the eastern part of the Yozgat Intrusive Complex were examined and their Raman spectroscopic characteristics were determined.

Raman spectra of melanites are identical to the andradite composition and have Raman shift peaks in the range of 170-1000 cm^{-1}. The melanites of the foid syenites exhibit strong Raman bands that are highly compatible with the reference spectra. The strong Raman peaks of the melanites examined are centered at 371, 879 and 522 cm^{-1}; moderate peaks are at 844, 819, 315 and 238 cm^{-1}; however the weaker peaks are observed at 997, 558, 495, 455, 329 and 264 cm^{-1} (Figure 3).

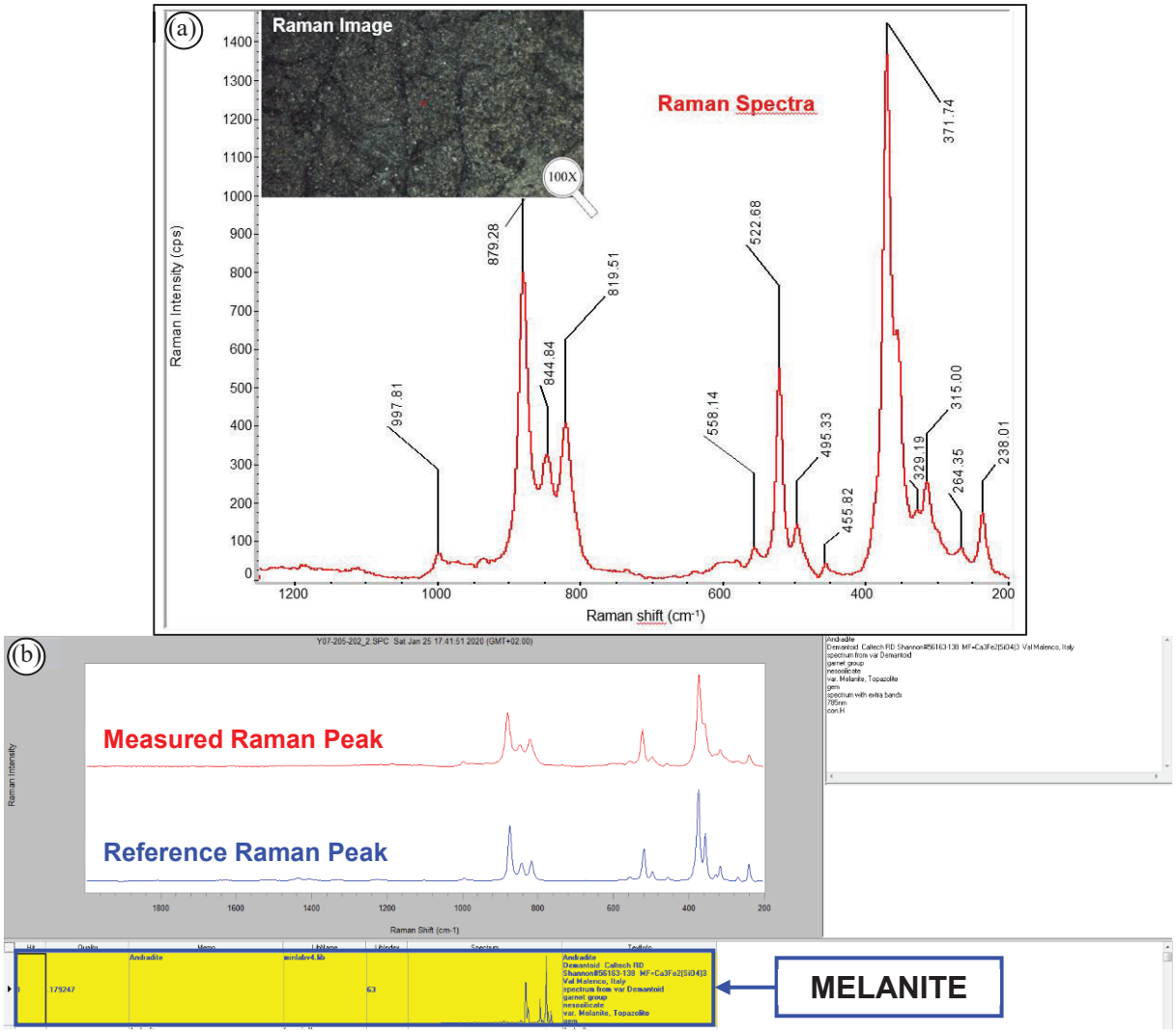

Figure 3. Raman spectroscopic characteristics of melanites in the foid syenites within the eastern part of the YIC ((a): Directly measured spectra, (b): Comparison of the measured peak and the reference peak).

The Raman spectra of the melanites are obtained in two main regions as (a) external vibration below 400 cm^{-1} and (b) internal vibrations above 400 cm^{-1} (Figure 4).

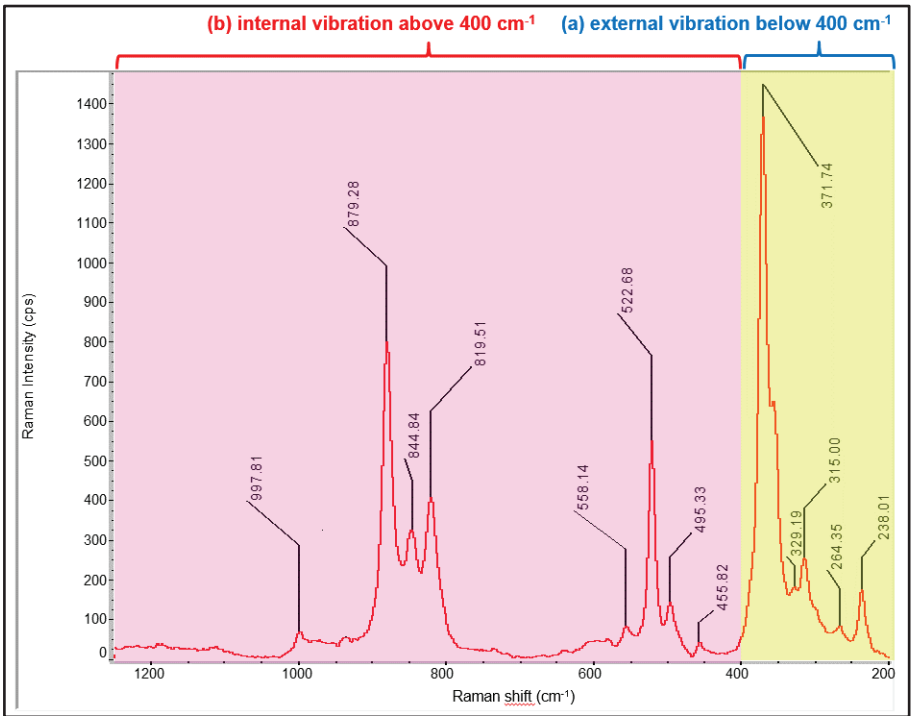

Figure 4. The main Raman spectral regions of melanites in the foid syenites within the eastern part of the YIC

Internal vibration spectra: Raman shifts observed in the spectral region between 750 and 1050 cm^{-1} originate from Si-O stretching vibrations, while Raman shifts observed in the spectral region between 400 and 600 cm^{-1} are due to bending modes of the Si-O (Figure 5).

External vibration spectra: Raman shifts observed in the spectral region between 300 and 400 cm^{-1} indicate rotational mode of SiO_4 tetrahedron $[R(SiO_4)^{4-}]$. Raman shifts observed in the spectral region between 200 and 300 cm^{-1} are related to translation mode of X-site cations $[T(X^{2+})]$ (Figure 5).

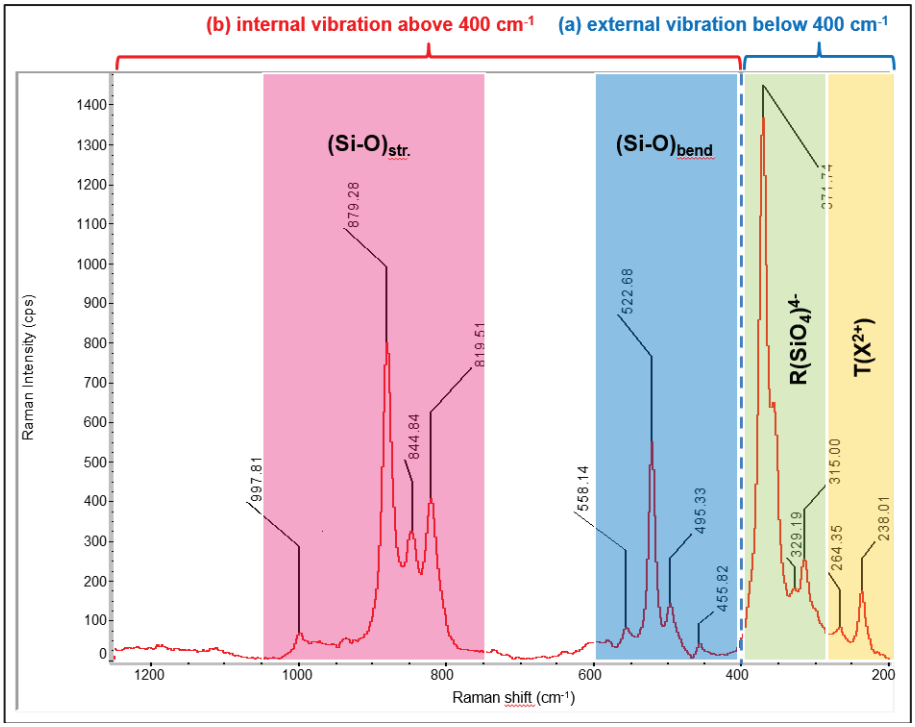

Figure 5. Mode assignments of the melanites in the foid syenites within the eastern part of the YIC

All symmetries, mode assignments and peak positions of the standard andradites (Hofmeister and Chopelas, 1991; Kolesov and Geiger, 1998) and the melanites in the foid syenites are reported in Table 1. The Raman spectra of the melanites in the foid syenites were compared to the standard andradite spectra and identified type of Raman shifts.

Table 1. Comparison of mode assignments and symmetries of the Raman active modes of the standard andradite type* and the melanites in the foid syenites.

Symmetry	Assignment	Andradite	Melanite in the foid syenites
F_{2g}	$(Si\text{-}O)_{str.}$	995	997
E_g	$(Si\text{-}O)_{str.}$	874	879
F_{2g}	$(Si\text{-}O)_{str.}$	842	844
F_{2g}	$(Si\text{-}O)_{str.}$	816	819
F_{2g}	$(Si\text{-}O)_{bend}$	593	
E_g	$(Si\text{-}O)_{bend}$	574	
F_{2g}	$(Si\text{-}O)_{bend}$	553	558
A_{1g}	$(Si\text{-}O)_{bend}$	516	522
F_{2g}	$(Si\text{-}O)_{bend}$	494	495
E_g	$(Si\text{-}O)_{bend}$	492	
F_{2g}	$(Si\text{-}O)_{bend}$	452	455
E_g	$(Si\text{-}O)_{bend}$	382	
A_{1g}	$R(SiO_4)^{4-}$	370	371
E_g	$R(SiO_4)^{4-}$	352	
F_{2g}	$R(SiO_4)^{4-}$	325	329
F_{2g}	$R(SiO_4)^{4-}$	312	315
E_g	$T(X^{2+})$	298	
F_{2g}	$T(X^{2+})$	264	264
F_{2g}	$T(X^{2+})$	236	238
E_g	$T(SiO_4)^{4-}$	174	
F_{2g}	$T(SiO_4)^{4-}$	174	

* Mode assignments and symmetries of the Raman active modes of the standard andradite type are taken from Hofmeister and Chopelas (1991); Kolesov and Geiger (1998).

CONCLUSION

Confocal Raman spectroscopic examinations in mineralogical determinations are quite compatible with and support optical microscopic examinations.

As a result of this study, the Raman spectra of the melanites in the foid syenites located in the eastern part of the Yozgat Intrusive Complex were examined, their Raman spectroscopic characteristics were determined and their importance in the crystallization process was revealed.

In this study, the foid-bearing syenites in the region have brown colored garnets and it has been determined that the compositions of these garnets fall into the andradite group and the species belong to the melanite group. It has been revealed that melanites are derived from silica unsaturated magmas and characterize alkaline magmas. It can be concluded that the results of petrographic and Raman spectra study overlap, detailed mineralogical definitions to be revealed by polarizing microscope studies, and comments on the magma character of the crystallized rock. It can be interpreted that the melanite-containing rocks are products formed due to the extension tectonism of the plate producing silica undersaturated magma due to the crustal thinning in the region.

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