DOKUZ EYLÜL UNIVERSITY
GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES

MINERALOGICAL AND GEMMOLOGICAL INVESTIGATION AND GENESIS OF OLTU STONE (CARBON BLACK)

by
Eyyüp Hikmet KINACI

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İZMİR

MINERALOGICAL AND GEMMOLOGICAL INVESTIGATION AND GENESIS OF OLTU STONE (CARBON BLACK)

A Thesis Submitted to the
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We have read the thesis entitled **"MINERALOGICAL AND GEMMOLOGICAL INVESTIGATION AND GENESIS OF OLTU STONE (CARBON BLACK)"** completed by **EYYÜP HİKMET KINACI** under supervision of **ASSOC. PROF. DR. MURAT HATİPOĞLU** and we certify that in our opinion it is fully adequate, in scope and in quality, as a thesis for the degree of Master of Science.

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MINERALOGICAL AND GEMMOLOGICAL INVESTIGATION AND GENESIS OF OLTU STONE (CARBON BLACK)

ABSTRACT

This study focuses on the microstructure and thermo gravimetric investigations for characterization of Oltu-stone (natural carbon black material) from the Oltu-Erzurum (Turkey) region (traditionally called in Turkey "Oltu-stone" or "black-amber"), which is of interest in several fields.

Many chemical and analytical investigations reveal essential fingerprints and genesis as well as provenance.

In the chemical analysis, LOI value of 97.8 per cent shows that the initial carbon amount is the highest. In addition, SiO_2 of 1.57 per cent, Fe_2O_3 of 0.50 per cent, and S of 0.32 per cent are unusual implication ratios. In the X-ray diffraction (XRD) pattern, the 4.20 and 3.78 angstrom centred two higher bands, and the 2.51, 2.28, 2.25 and 2.12 angstrom centred four relative lower bands are specific. Particle sizes are certified by 3-D and 2-D graphics of atomic force microscope (AFM), the grain sizes of the matrix components display a libration with a minimum of 900 nm and a maximum of 1.2 micrometer. In the simultaneous differential thermo gravimetric and thermo gravimetric (DTA/TGA) glow curves, main thermo gravimetric weight loss is about 52 per cent at 316.5 centigrade degree, and the last weight loss is about 2 per cent at 1400 centigrade degree. Finally, total weight loss is 57 per cent. This result show having relatively higher resistance of the material components against to the over-heats. The dispersive confocal (532 nm green laser) micro-Raman spectra (DCμRS), recorded between 50 and 3200 cm^{-1}, show that these measurements in a wide spectral range are the basis for effective characterization and identification with respect to analogous carbonaceous materials. Two higher main peaks at 1346 and 1585 cm^{-1} are characteristic of the crystalline (graphite) carbon regions, whereas the weaker ones at 2654 and 2904 cm^{-1} are assigned to amorphous (soot or charcoal) carbon regions on the surface. In addition, as the main inclusions, while the

enhanced background between 200 and 500 cm^{-1} in these spectra could be related to SiO_2, the higher peak at about 100 cm^{-1} could be related to Fe_2O.

As regarding to genesis, these results of the further investigations show that carbonaceous Oltu-stone material with a specific gravity of 1.317 is not an amorphous organic jet material occurred from a wood. In fact, it is an inorganic material occurred from carbonaceous para-crystallites interbedded with marl strata during diagenesis in a sedimentary deep-sea deposition. Hence, we state that the preliminary origin of natural carbon black riches to the mineral graphite family.

Keywords: Natural Turkish carbon black, Oltu-stone, graphite, Erzurum-Turkey.

OLTU TAŞININ (KARBON KARASI) MİNERALOJİKSEL VE GEMOLOJİKSEL ÖZELLİKLERİ İLE OLUŞUM KÖKENİ

ÖZ

Bu çalışma, birçok sahada ilgi odağı olan ve geleneksel olarak Türkiye'de "Oltu-taşı" yada "siyah-amber" olarak adlandırılan, Oltu-Erzurum bölgesinden Oltu-taşının (doğal karbon karası materyali) karakterizasyonu için mikro yapı ve termo gravimetrik incelemeleri üzerine odaklanmıştır.

Çok sayıda kimyasal ve analitik incelemeler, büyük önem taşıyan karakteristik verileri ve oluşum kökenini ile aynı zamanda oluşum ortamını ortaya çıkartmaktadır.

Kimyasal analizlerde, yüzde 97.8'lik LOI değeri ilksel karbon miktarının çok yüksek olduğunu gösterir. İlaveten, yüzde 1.57'lik SiO_2, yüzde 0.50 Fe_2O_3 ve yüzde 0.32'lik S alışılmamış içerimsel oranlardır. X-ışını saçınım (XRD) kalıbında, 4.20 ve 3.78 angstromlarda merkezlenmiş iki çok yüksek band ve 2.51, 2.28, 2.25 ve 2.12 angstromlarda merkezlenmiş dört göreceli alçak band, özgündür. Parçacık boyutları, atomik güç mikroskobunun (AFM) 3-D ve 2-D grafiklerin vasıtasıyla onaylanmaktadır. Matriks bileşenlerinin dane boyutları bir minimum 900 nanometre ve bir maksimum 1.2 mikrometreye sahip bir sallantıyı göstermektedir. Eş zamanlı diferansiyel termo gravimetric ve thermo gravimetric (DTA/TGA) kızdırma eğrilerinde, ana termo gravimetric ağırlık kaybı 316.5 santigrat derecede yaklaşık yüzde 52 ve son ağırlık kaybı 1400 santigrat derecede yaklaşık yüzde 2 olup, sonuçta toplam ağırlık kaybı yüzde 57'dir. Bu sonuç, materyal bileşenlerinin aşırı sıcaklıklara karşı göreceli daha yüksek dirence sahip olduklarını gösterir. 50 ve 3200 cm^{-1} aralığında kaydedilmiş, saçınımsal konfokal (532 nanometre yeşil lazer) mikro-Raman ((DCμRS) spektraları, geniş bir spektral aralıktaki bu ölçümlerin benzer karbonsu materyallerin karşılıklı tanımlanması ve etkili karakterizyonu için esas oluşturduğunu göstermektedir. 1346 ve 1585 cm^{-1}'deki iki çok yüksek ana pik kristalin (grafit) karbon bölgelerinin karakteristiğidir. Buna karşılık 2654 and 2904 cm^{-1}'deki zayıf olanlar, yüzey üzerindeki amorf (kurum yada odun kömürü) karbon

bölgelerine atfedilmektedir. İlaveten, ana kapanımlar olarak spektralarda 200 ve 500 cm^{-1}'lerde işlenmiş zemin, SiO_2 ye ilişkilendirilebilirken, 100 cm^{-1}'deki göreceli daha yüksek pik Fe_2O ye ilişkilendirilebilir.

Kökene ilişkin olarak, ileri araştırmaların bu sonuçları göstermektedir ki, özgül ağırlığı 1.317 olan karbonsu Oltu-taşı materyali bir odundan oluşmuş amorf organik bir jet materyali değildir. Aslında bir sedimantar derin deniz depolanması sırasında diyajenez (düşük dereceli metamorfizma) sürecinde marn katmanları ile ara tabakalanmış karbonsu yarı kristalitlerden oluşmuş inorganik bir materyaldir. Bu yüzden, diyebiliriz ki, doğal karbon karasının ilksel kökeni grafit mineral ailesine uzanır.

Anahtar sözcükler: Doğal Türk karbon karası, Oltu-taşı, grafit, Erzurum-Turkiye.

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CHAPTER ONE
INTRODUCTION

The toughness, durability, specific gravity, and coloration of carbonaceous compact black material from different locations in the world (e.g. Turkey, Georgia, and Armenia) are highly variable because of their genera and deposition conditions. However, those of Oltu-Erzurum (Turkey) region are characteristic and unique. The material which certified as a kind of natural carbon black (Hatipoğlu et al., 2012) is present some unusual mineralogical data. Therefore, subtle differences between carbon blacks can be attributed to their genesis (Lahaye and Prado, 1981; Wang and Wolff, 1993; Donnet, 1994; Ungar et al., 2002; Ungar et al., 2005). Carbon blacks are generally used as filler in rubber production to modify the mechanical properties of the tire (Donnet, 1994; Clague et al., 1999; Hjelm et al., 2000). The internal structure of carbon black aggregates is not well understood. Graphite-like, quasicrystalline domains, in which basal planes are parallel but angularly distorted and the spacing between the layers is different from that of pure graphite, have been detected in carbon black particles. Therefore, those structures as intermediate between crystalline and amorphous materials have been identified (Donnet, 1994).

In Turkey, a natural compact carbonaceous black material, which is traditionally known as “Oltu stone”, has been easily carved only as gem objects in the jewellery market in the Oltu-Erzurum region (northern Anatolia) since the 18th century (Figure 1.1). Oltu-stone is used mostly to make ornaments such as rings, earrings, necklaces, bracelets, tiepins, pipes, studs, cigarette holders, prayer beads, generally in combination with silver (Zengin, 1956; Çiftçi et al., 2002; Karayiğit et al., 2002; Çiftçi et al., 2004; Karayiğit, 2007; Hatipoğlu et al., 2012; Kalkan et al., 2012) (Figure 1.2). Turkish governmental bodies such as, DÖSİMM of The Ministry of Culture and Tourism, (Traditional Turkish Handicrafts Foundation), nongovernmental organisations and many other institutions have been trying to preserve and develop Oltu-stone handicrafts (Figures 1.3 and 1.4). Today, as a popular hobby item, Oltu-stones have assumed decorative meanings beyond their use in jewellery.

Figure 1.1 Oltu stone has been easily carved only in the Oltu-Erzurum region (northern Anatolia) since the 18th century. The rough Oltu-stones are cut and polish by local artisans and craftsmen using some basic equipment, such as, electric lathe, polishing wheel, drill and some hand tools, such as, steel knife, file, sandpaper and turned suitable for working.

Figure 1.2 Oltu stone has been easily carved only as gem objects (such as rings, earrings, necklaces, bracelets, tiepins, pipes, studs, cigarette holders, prayer beads, and generally in combination with silver) in the jewellery market.

Figure 1.3 Turkish governmental bodies, nongovernmental organisations and many other institutions have been trying to preserve and develop Oltu-stone handicrafts. These craftsmen process cuttinf and carving in desired form and polished to manufacture rosery and various decorative ornaments and utensils.

Figure 1.4 Typical Oltu-stone cutting workshops in the Oltu district. The workshops are still traditional cutting and polishing methods.

On the other hand, many studies on carbon blacks have been performed by different methods in the last three decades (Bansal and Donnet, 1993; Gruber et al., 1993; Wang and Wolff, 1993; Donnet, 1994; Jawhari et al., 1995; Bertrand and Weng, 1999; Hjelm et al., 2000; Zerda et al., 2000; Lin, 2002; Probst and Grivei, 2002) for a better determination of its chemical and physical properties, also in order to distinguish inorganic carbon blacks from organic jet and/or carbon-like materials in archaeological and gemmological science (Hunter et al., 1993; Gruber et al., 1994; Hatipoğlu et al., 2012). Carbon black surface and bulk structures were accurately studied by methodologies like X-ray diffraction, neutron scattering (Franklin, 1950; Clague et al., 1999; Hjelm et al., 2000), Raman spectroscopy (Gruber et al.,1993 and 1994; Jawhari et al.,1995; Hatipoğlu et al., 2012; Hauptman et al., 2012), TOF-SIMS (Time-of-Flight Secondary Ion Mass Spectrometry) and XPS (X-ray Photoelectron Spectroscopy) (Bertrand and Weng, 1999), so providing a model of carbon black aggregate that is widely accepted today: according to this, carbon black is a material composed essentially of elemental carbon in the form of quasi-spherical particles that are fused together into aggregates (Donnet, 1994; Clague et al., 1999).

The presence of two different carbon structures on the carbon black surface except some inclusion minerals has been observed by X-Ray diffraction (Franklin, 1950, Donnet, 1994), and Raman spectroscopy confirmed the presence of at least two different structures on carbon black (Gruber et al.,1993 and 1994; Jawhari et al.,1995; Zerda et al., 2000; Ungar et al., 2005; Hatipoğlu et al., 2012): one of these has a structure similar to graphite, and the second to unknown amorphous carbon.

It is well known that the Raman probe offers an approach to nanomaterials and amorphous compounds, in particular in the case of imperfect crystals built of strong covalent bonds (Deckert et al., 2008; Slodczyk and Colomban, 2010). A given vibration always appears in the same region, its exact position giving information about the local environment, both in the crystalline and amorphous states (Gouadec and Colomban, 2007). The micro-Raman spectroscopy has been widely used to study carbon allotropes (diamond, graphite, fullerenes, nanotubes). It is indeed one of the few techniques sensitive to the full range of structural states present in this class of

materials, from perfectly crystalline to amorphous. Gouadec and Colomban (2007) have stated that the common crystalline phases of carbon yield very simple spectra: diamond (sp^3 hybridisation) peaks at 1332 cm^{-1} (single mode of T_{2g} symmetry) whereas graphite (sp^2 hybridisation) has doubly degenerate E_{2g} modes at 42 and 1582 cm^{-1} (Tuinstra and Koening, 1970). The latter is referred to as G band and corresponds to vibrations in the graphene planes (whose crystalline quality can be assessed by the width of the G band) whereas the former corresponds to weak inter-planar Van der Waals interactions (this is the reason for its low energy) (Brown and Altermatt, 1985). Two additional modes D and D' (D stands for ‘‘disorder’’) appear whenever flaws are created, grain size is reduced or graphene planes are bent (Lewis and Edwards, 2001; Gouadec and Colomban, 2007).

In the past, some scientific and advertising papers have been published on the Oltu-stone from the Erzurum (Turkey) region, even though this material has been called jet or jet-coal in those studies (Zengin, 1956; Çiftçi et al., 2002; Çiftçi et al., 2004; Karayiğit et al., 2002; Karayiğit, 2007; Kalkan et al., 2012). Actually, Hunter et al. (1993) reported upon the characterisation of jet, in comparison with similar materials, by means of several physico-chemical techniques, among others Raman spectroscopy; according to these authors, spectra of different materials (jet, lignite and cannel coal) did not exhibit significant differences. On the other hand, Smith and Clark (2004) noticed within an important review on Raman microscopy in archaeological science that the work of Hunter et al. (1993) was done before highly sensitive Raman apparatus became available. However, since the paper of Smith and Clark (2004), no further information on this subject appeared in our knowledge.

In this study, we propose essential fingerprints and genesis of Oltu-stone being a natural carbon black material, in case of provenance characterization and identification using many mineralogical and chemical methods, for the possible industrial applications beyond jewellery, made possible by its huge reserves.

CHAPTER TWO
MATERIALS AND METHODS

The investigated Oltu-stone material is a natural carbonaceous material. The rough Oltu-stone is generally of dull-bright black color, but sometimes it is blackish brown, grey, or greenish; black samples. When rubbed, the Oltu-stone attracts, by way of static electricity, light substances such as dust.

Elemental composition and implications of the representative Oltu-stone samples were determined. In this analyses, the following analytical procedures were performed; The instrument LECO for total carbon (C-IR07)-Leco, the instrument LECO for total sulphur (S-IR08)-Leco, the instrument ICP-AES for Whole rock package (ME-ICP06)-ICP-AES, the instrument WST-SEQ for loss on initiation at 1000 ^{o}C (OA-GRA05), the instrument ICP-MS for 38 element fusion (ME-MS81)-ICP-MS, and the instrument ICP-AES for total calculation for ICP06 (TOT-ICP06). These analyses were certified with the code number "IZ11205067", under contract by the accredited ALS Chemex Laboratory in Canada.

The specific gravity (SG) values of the many Oltu-stone samples were measured in this study using an electronic balance scale (measurement sensitivity of 0.001) with an SG kit, based on the formula ($SG = W_{air} / W_{air} - W_{water}$). The test was performed in the DGL-Gemmological Testing Laboratory at Dokuz Eylül University.

The base building components of the representative Oltu-stone samples were detected using X-ray powder diffraction analysis, using a Cubi-XRD device with a Cu tube and a graphic monochromotor. The samples were analyzed with Cu radiation and a 0.3 mm collimator at atmospheric pressure for 10 minutes each, in the range between 5° and 70° (2-theta). The d-spacing [Å] diffraction matching of the constituent minerals obtained using the comparative matching technique is based on the positions of peaks with relative intensities [$\%(I/I_o)>1$], 2-theta values below 70°, and a tolerance range of ±0.01. X-ray powder diffraction patterns were taken in the Research Laboratory of the Batı Anadolu Cement Factory in İzmir.

Polarizing microscope images of thin sections of the representative Oltu-stone samples were obtained by using an Olympus BX41 binocular polarizing microscope with a high-intensity 6V, 30W halogen light source combined with U-CPA and U-OPA optical systems. For the digital images, the microscopic magnification (MM) was 4x (resulting from 0.4x objective and 10x ocular) and 10x (1x objective and 10x ocular) under crossed nicols (+N) (active polarizer and analyzer).

Internal structures of the representative Oltu-stone samples at different magnifications up to 100.000x were observed using a Philips XL 30S FEG (Field Transmission Gun) scanning electron microscope (SEM), after they were coated with a 5 nm thick gold powder. These images were also obtained in the Material Investigation Centre of İzmir Institute of Technology.

An atomic force microscope (AFM) device, the Nanosurf easyScan-2 of nanoScience instruments with a 70 micron scanning range, was used to observe: the surface morphologies of the representative Oltu-stone samples. An AFM is a mechanical imaging instrument that measures the three dimensional topography as well as the physical properties of a surface with a sharpened probe. In addition, the grain sizes of the samples were measured precisely. Because the AFM does not use electromagnetic radiation, such as photon or electron beams, to create an image, the precise particle sizes of any material can be measured.

Differential thermal analysis and thermo gravimetric analysis (DTA/TGA) of the representative Oltu-stone samples were conducted by using a thermal analysis system (Shimadzu TDG-60H). The DTA/TGA device was used to determine the changes in weight and heat energy enthalpy against temperature in the samples. In the patterns, the change of the DTA is in millivolts, and the change of the TGA is in milligrams. Analyses were performed under nitrogen atmosphere. The samples were approximately 6 mg in weight, and were heated from room temperature (about 25 ^{o}C) up to 1400°C at a constant rate of 10°C/min to observe their heating behaviour. The drift concerning the mass gain observed in the TGA glow curves (the dotted red

lines on the patterns) is the typical effect of buoyancy, so the mass gain is an experimental artefact exhibited by the thermobalance instrumentation. Therefore, the mass loss data obtained from the TGA curves were corrected to eliminate the buoyancy drift of the atmosphere gas. In fact, the only way to remove the data of this buoyancy component is to decrease the heating rate and increase the sample mass. However, in order to increase the sample amount is not possible because of the small sample crucible of the device used in the study. On the other hand, Oltu-stone samples have some characteristic mineral inclusions, Therefore, the endotherms on the mass gain curves (the dotted blue lines on the patterns) of the DTA glow curves may also be an artefact due to the shift in baseline as the thermal mass of the specimen is reduced by loss of carboniferous material. Thus, the DTA curves have also been corrected in the straight blue line as well as in the endotherm data.

Massive and unoriented samples of Oltu-stone were placed on the stage of an Olympus BM-41 microscope, equipped with 10x and 50x objectives and part of a HORIBA Jobin Yvon Scientific XPLORA dispersive (visible) confocal micro-Raman spectrometer with a high throughput integrated spectrograph, which also includes a monochromator, a filter system and a charge-coupled device (CCD). Raman spectra were excited by a He–Ne laser (532 nm) at a resolution of 1 cm^{-1} in the range between 4000 and 50 cm^{-1}. The micro-Raman analyses were performed on a dark background at room temperature. Repeated acquisition using the highest magnification was accumulated to improve the signal-to-noise ratio. Spectra were calibrated using the 520.5 cm^{-1} line of a silicon wafer. Spectral manipulation as a baseline adjustment was carried out using the software of the device. Spectral details are as the followings; objective: x50, filter: 100%, exposition: 10, accumulation: 1x2, laser: 532.06, spectro: auto, hole: 500, silt: 100, grating: 1800T, ICS correction: on, and power: 25 mW at sample. The Raman analysis was carried out in the Gemmological Testing Laboratory at the İzmir Multidisciplinary Vocational School of Dokuz Eylül University.

CHAPTER THREE
RESULTS AND DISCUSSION

3.1 Provenance, Mining, Appearance, Geological Setting, and Origin

The investigation material (Oltu-stone) of this study has been mined mainly from the vicinity of the Dutlu Mountains in the Oltu-Erzurum region of Turkey for about one century (Figure 3.1). The material is excavated especially in Dutlu, Gökçedere, Güzelsu, and Günlüce villages (Figure 3.2).

There are approximately 600 quarries. Out of the total 287 quarries in the central Dutlu region, about 120 quarries are still being worked (Figure 3.3). The location finding process for the Oltu-stone extracting gallery is carried out based on experience with field observations. The material is mined from mountainous areas perpendicular to the general surface with galleries of 70-80 cm in diameter where only two or three miners can work. Some basic apparatus, such as digging, short-handled shovel, hammer and chisel are used for the gallery creating process. When galleries continue to progress, the generated waste material are brought out from galleries by using transport tools with four-wheeled wooden which can be pulled by rope. When the galleries reach up to 150 m or unexpected situations occur preventing it to work in the gallery, it is abandoned (Zengin, 1956; Çiftçi et al., 2002; Karayiğit et al., 2002; Çiftçi et al., 2004; Karayiğit, 2007; Bilgin et al., 2011; Kalkan et al., 2012) (Figures 3.3 and 3.4). This material is deposited as stratiform strata alternated with marn strata between about 0.5 and 80 cm in thickness. However, these Oltu-stone strata are always no longer thoroughly in the unit. They are mainly founded in about 20-30 cm in length (Zengin, 1956) (Figure 3.5A).

The material that certified as a kind of carbon black (Hatipoğlu et al., 2012) from the Oltu-Erzurum (Turkey) region is unique, and has some unusual mineralogical data. The rough Oltu-stone is generally of dull-bright black color, but sometimes it is blackish brown, grey, or greenish; black samples (Figure 3.5B). This stone discharges the static electricity in the human body and in that way it is somewhat of a

remedy for stress. Oltu-stone stays shiny as long as it is used and it does not react with human sweat and leaves no traces on the skin.

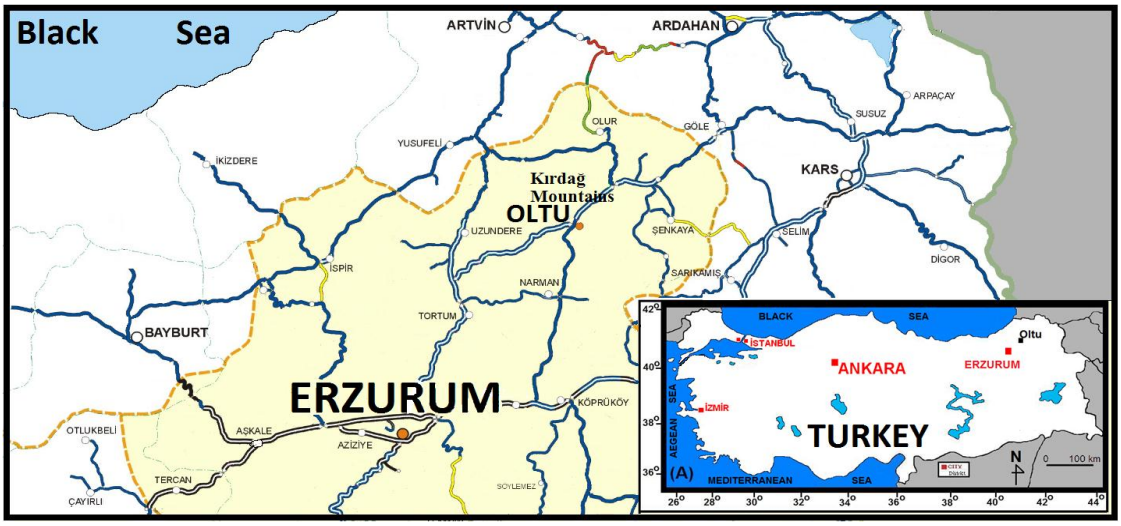

Figure 3.1 The location map showing the Oltu-Erzurum region in Turkey, in which there are approximately 600 quarries including the carbon black material (traditionally called in Turkish as Oltu-stone). The Oltu-stone has been mined mainly from the vicinity of the Dutlu Mountains in the Oltu region of Erzurum city for about one century.

Figure 3.2 Satellite map showing the nearest villages to Oltu-stone pits.

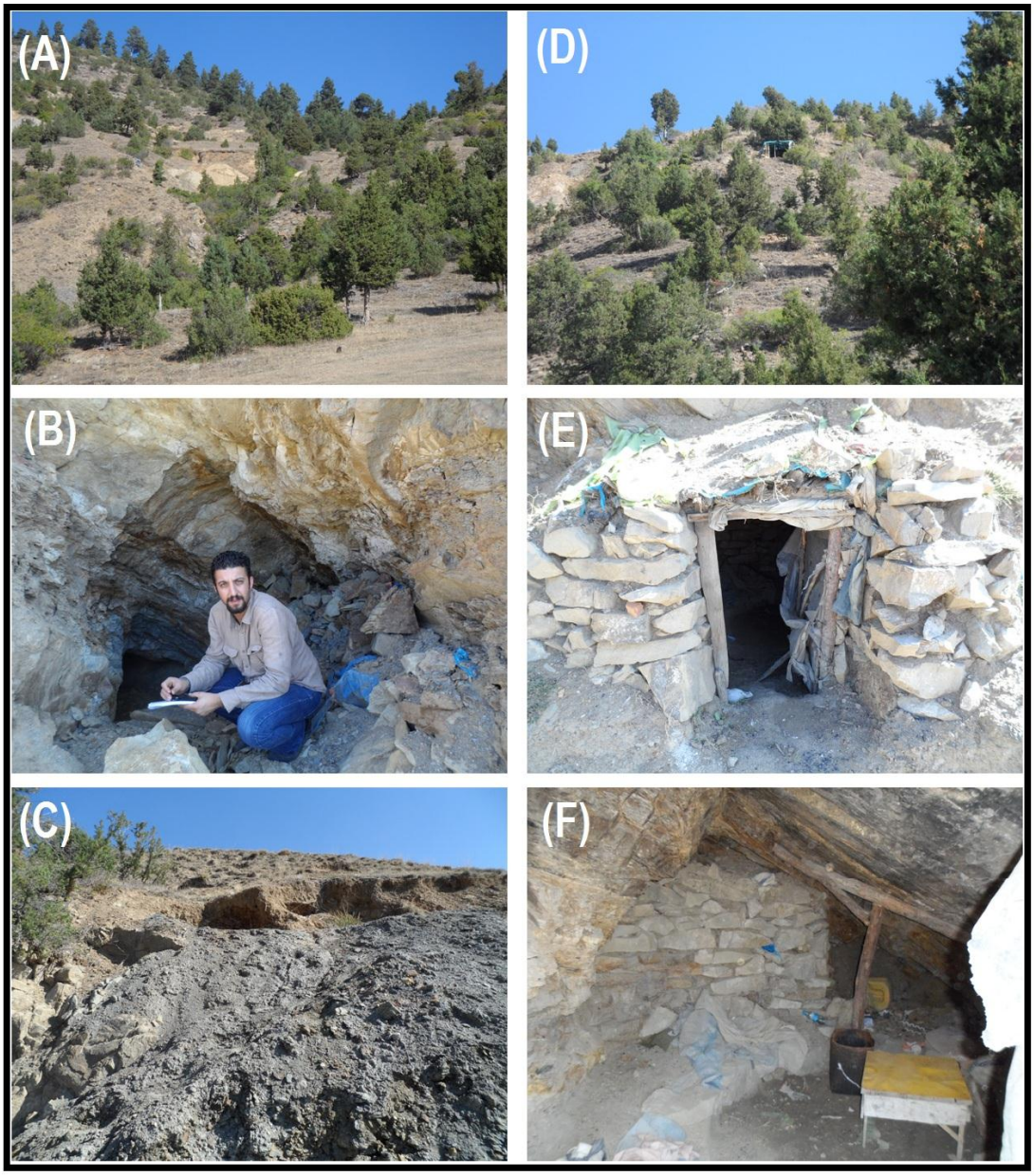

Figure 3.3 Oltu-stone is mined from mountainous areas perpendicular to the general surface. Three different viewings of the narrow pits **(A)**, **(B)**, **(C),** and relatively large galleries **(D)**, **(E)**, **(F),** opened in the surrounding rock. When the galleries reach up to 150 m or unexpected situations occur preventing it to work in the gallery, it is abandoned. The productions of Oltu-stones are carried out by non-technological methods in the underground galleries.

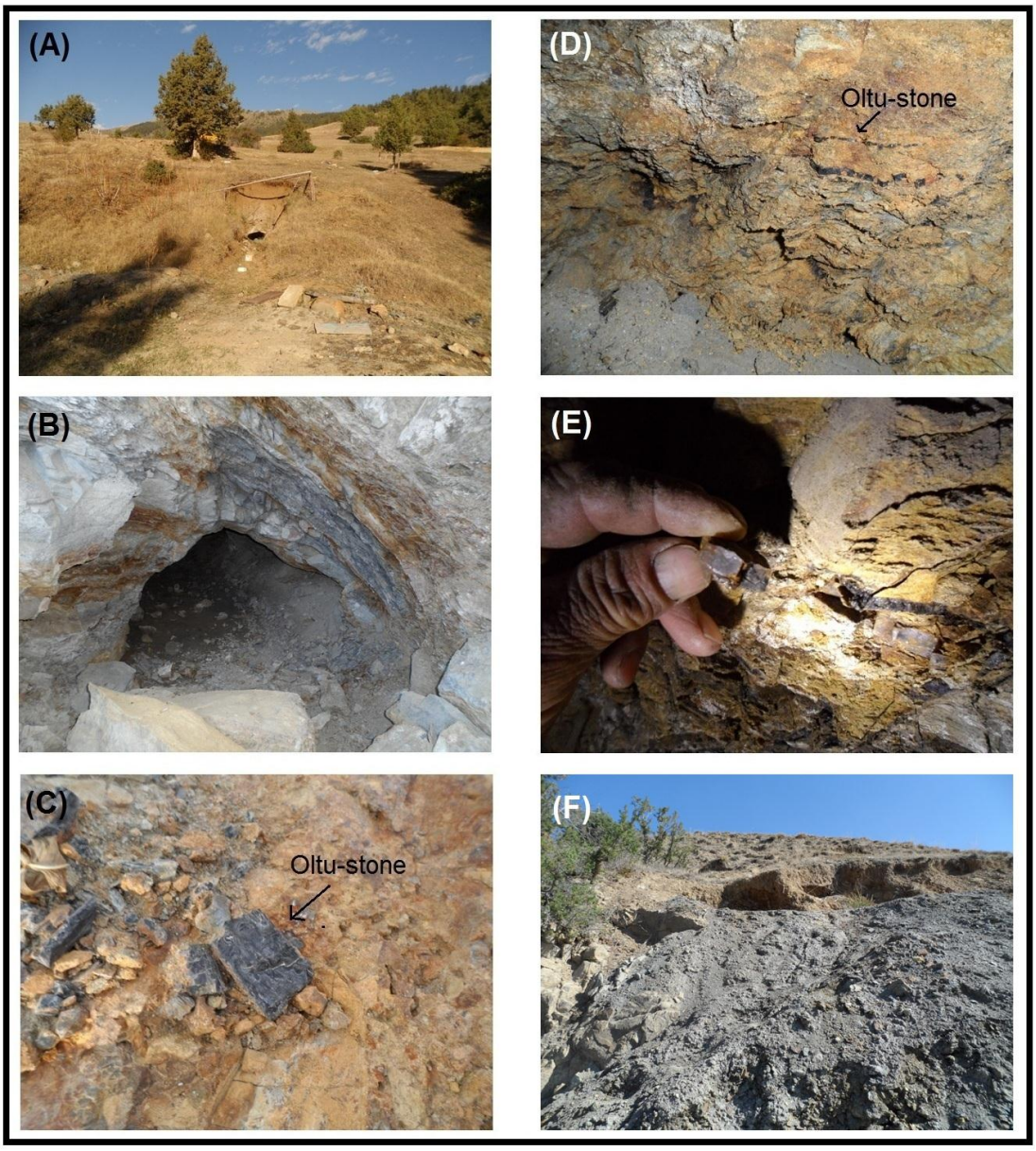

Figure 3.4 Out of the total 287 quarries in the central Dutlu region**,** about 120 quarries are still being worked **(A)**, **(B)**, and **(C)**. The material is mined from mountainous areas perpendicular to the general surface with galleries of 70-80 cm in diameter where only two or three miners can work **(D)** and **(E)**. This material is deposited as stratiform strata with between about 0.5 and 80 cm in thickness. However, these Oltu-stone strata are no longer thoroughly in the unit. They are founded in about 20-30 cm in length **(F)**. Sedimentary sequence including Oltu-stone comprises fine-grained marl and limestone at the top and coarse-grained conglomerate at the bottom. On the other hand, this Tertiary aged sedimentary sequence overlies a Jurassic-Cretaceous aged dacitic volcanic unit.

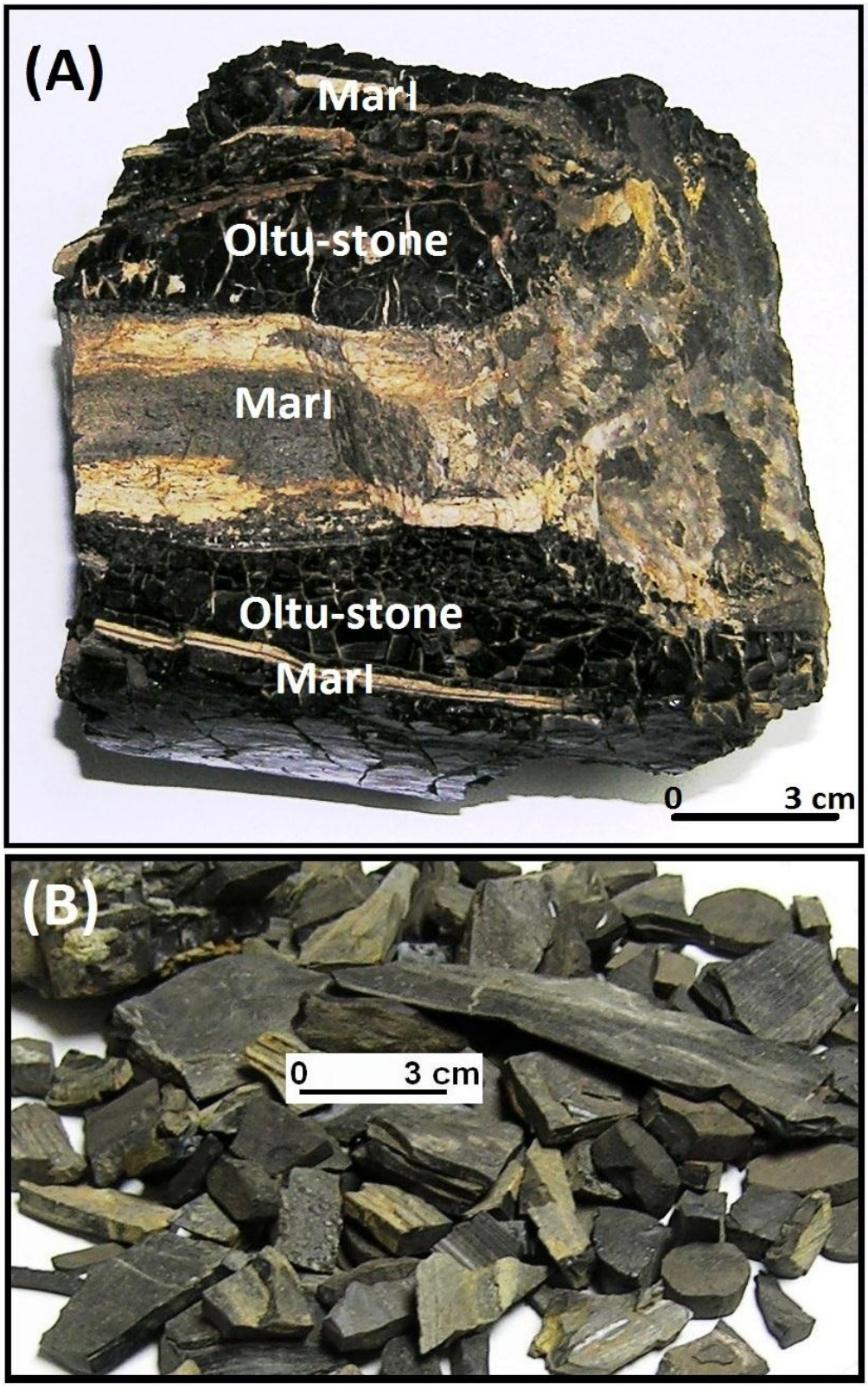

Figure 3.5 A block including Oltu-stone material and surrounding marl rock alternately **(A)**. The loose rough Oltu-stones **(B)**.

As a result of detailed field observations, it can be stated that The Oltu region includes a sedimentational basin and is underlain by volcanic rocks. The Oltu-stone strata are interbedded in the Tertiary aged marl unit (Bozkuş, 1991; Kalkan et al., 2012). In fact, sedimentary sequence including Oltu-stone comprises fine-grained marl and limestone at the top and coarse-grained conglomerate at the bottom. On the other hand, this sedimentary sequence overlies a Jurassic-Cretaceous aged dacitic volcanic unit (Zengin, 1956; Karayiğit et al., 2002; Karayiğit, 2007; Kalkan et al., 2012). However, in fact, there is no modern review of geological properties of the Oltu-stone and Oltu-stone bearing deposits. The last paper is seems to be the most plausible geological study (Kalkan et al., 2012) (Figure 3.6).

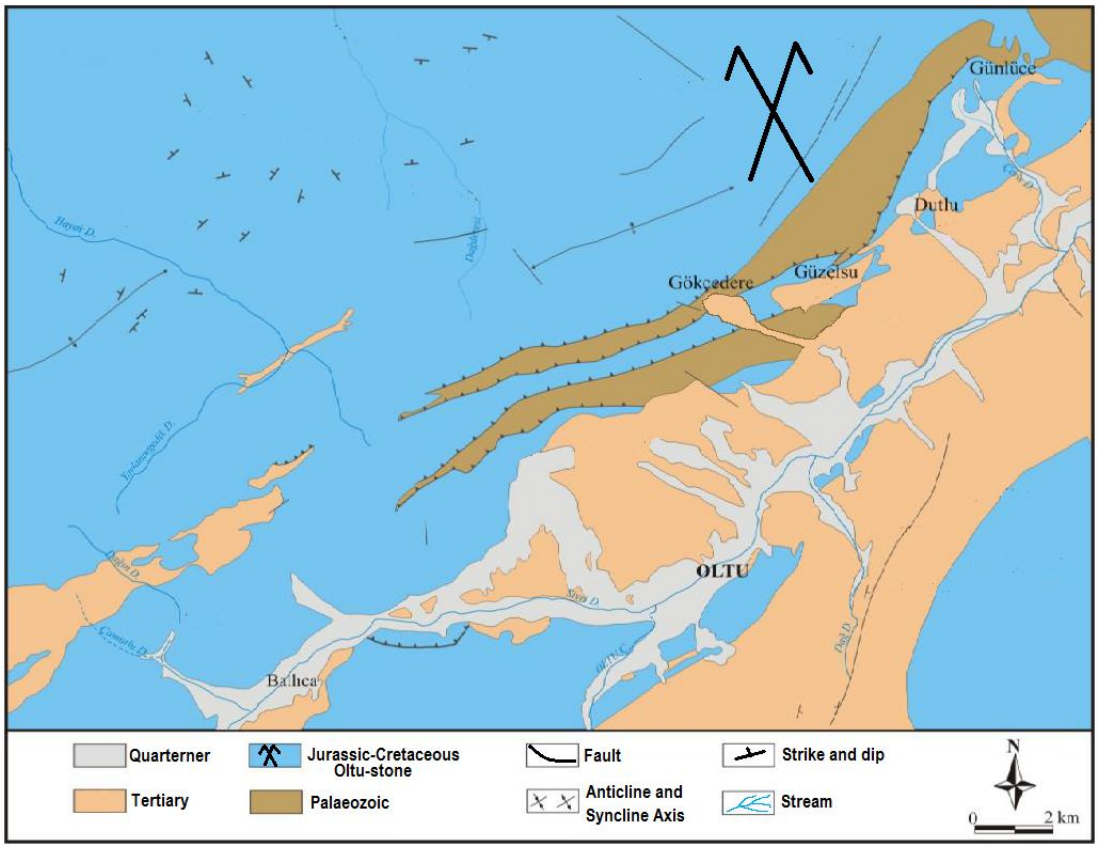

Figure 3.6 Simplified geological map of the Oltu vicinity, comprising Gökçedere, Güzelsu, Dutlu, and Günlüce villages (modified from Bozkuş, 1991, Konak et al., 2001, and Kalkan et al., 2012).

The region comprising Oltu-stone bearing deposit is located in the Northeastern Anatolian Region between the Pontides belt (North Anatolian Mountain Ranges) in the North and the Anatolides belt (Inner Anatolian Mountain Ranges). The tectonic movements become effective on the forming of Northeastern Anatolian Region and this region is under control of compressive stress with North-South direction, since the Cretaceous (Şengör et al., 1985; Koçyiğit et al., 1985). This formation begins in general clastic sediments with coarse particles in the southern slope of Dutlu Mountains (Oltu, Erzurum). In this region, pelagic pebbles with lenticular geometry that are poorly sorted are observed in the lower levels of sequence (Bozkuş, 1991; Konak et al., 2001; Alkan et al., 2012).

Oltu-stone is a material composed essentially of elemental carbon in the form of quasi-spherical particles that are fused together into aggregates (Bansal and Donnet, 1993; Clague et al., 1999). The geochemical formation of Oltu-stone can be considered to incorporate many of the features common to the thermal oxidative decomposition processes in a sedimentation basin during the geological period. It is obtained by partial combustion or thermal decomposition of hydrocarbons. As a result, it can be state that the carbonaceous Oltu-stone materials are not an organic jet material occurred from a wood inferred by Zengin (1956), Çiftçi et al. (2002), Karayiğit et al. (2002), Çiftçi et al. (2004), and Karayiğit, (2007). In fact, it is an inorganic material occurred from para-crystallites alternated with marl strata in a sedimentary deposition. Hence, we state that the preliminary origin of natural carbon black riches to the mineral graphite (Tuinstra and Koenig, 1970; Hatipoğlu et al., 2012).

3.2 Chemistry

The results of the chemical analysis of the representative Oltu-stone are given in Table 3.1.

Two important elements - Carbon as over 50% and sulphur as about 0.32% are become clear. If it is considered 97.8% of LOI value, it can be that initial carbon

amount is the relatively highest in Oltu-stone. This value is similar to those of synthetic carbon black varieties published before; such as, 97.7% for “unspecified”, 96.5% for “vulcan XC 72R”, 98.4% for “cabot fluffy”, and 95.5% for “regal 600” (Clague et al., 1999).

It is seen that very unusual data in the analyses is the high concentration existence of silica (SiO_2: 1.75). In addition, higher Ba (8.8 ppm) and V (175 ppm) concentrations are interesting for a coal material. It is noted that the abundance of main radioactive elements, such as Sr (10.5 ppm), Th (0.38 ppm), U (023 ppm), and Zr (67 ppm), are high and unusual. This abundance of the radioactive elements is attributed to deep-sea sedimentation and diagenesis. All these chemical evidences show that carbonaceous Oltu-stone material is not an organic jet material transformed from a wood. They sign to an inorganic carbon material. Clague and his colleagues (1999) found the similar values to those of synthetic carbon blacks used in experiments on diesel engine soot (Clague et al., 1999).

Table 3.1 Chemical bulk and trace element analyses of the representative Oltu-stone.

Bulk	Method	Detection limits	**Oltu-stone**	Trace	Method	Detection limits	**Oltu-stone**
SiO_2	ME-ICP06	0.01 %	1.57	Ag	ME-MS81	1 ppm	<1
Al_2O_3	ME-ICP06	0.01 %	0.20	Ba	ME-MS81	0.5 ppm	8.8
Fe_2O_3	ME-ICP06	0.01 %	0.50	Ce	ME-MS81	0.5 ppm	2.5
CaO	ME-ICP06	0.01 %	0.28	Co	ME-MS81	0.5 ppm	3.6
MgO	ME-ICP06	0.01 %	0.06	Cr	ME-MS81	10 ppm	20
Na_2O	ME-ICP06	0.01 %	0.05	Cs	ME-MS81	0.01 ppm	0.13
K_2O	ME-ICP06	0.01 %	0.04	Cu	ME-MS81	5 ppm	**<5**
Cr_2O_3	ME-ICP06	0.01 %	<0.01	Dy	ME-MS81	0.05 ppm	0.91
TiO_2	ME-ICP06	0.01 %	0.03	Er	ME-MS81	0.03 ppm	0.46
MnO	ME-ICP06	0.01 %	0.01	Eu	ME-MS81	0.03 ppm	0.16
P_2O_5	ME-ICP06	0.001 %	0.08	Ga	ME-MS81	0.1 ppm	1.1
SrO	ME-ICP06	0.01 %	<0.01	Gd	ME-MS81	0.05 ppm	0.83
BaO	ME-ICP06	0.01 %	<0.01	Hf	ME-MS81	0.2 ppm	0.7
				Ho	ME-MS81	0.01 ppm	0.19
LOI	OA-GRA05	0.01 %	97.8	La	ME-MS81	0.5 ppm	1
Total	TOT-ICP06	0.01 %	**100.5**	Lu	ME-MS81	0.01 ppm	0.06

Table 3.1 (continue)							
				Mo	ME-MS81	2 ppm	<2
C	C-IR07	0.01%	>50	Nb	ME-MS81	0.2	3.2
S	S-IR08	0.01%	0.32	Nd	ME-MS81	0.1 ppm	1.4
				Ni	ME-MS81	5 ppm	6
				Pb	ME-MS81	5 ppm	<5
				Pr	ME-MS81	0.03 ppm	0.32
				Rb	ME-MS81	0.2 ppm	2.5
				Sm	ME-MS81	0.03 ppm	0.46
				Sn	ME-MS81	1 ppm	<1
				Sr	ME-MS81	0.1 ppm	10.5
				Ta	ME-MS81	0.1 ppm	<0.1
				Tb	ME-MS81	0.01 ppm	0.14
				Th	ME-MS81	0.05 ppm	0.38
				Tl	ME-MS81	0.5 ppm	<0.5
				Tm	ME-MS81	0.01 ppm	0.08
				U	ME-MS81	0.05 ppm	0.23
				V	ME-MS81	5 ppm	175
				W	ME-MS81	1 ppm	4
				Y	ME-MS81	0.5 ppm	6
				Yb	ME-MS81	0.03 ppm	0.40
				Zn	ME-MS81	5 ppm	8
				Zr	ME-MS81	2 ppm	67

3.3 Specific Gravity

The hydrostatic balance (HB) method (Figure 3.7) was used to analyse the Oltu-stone samples. The values based on the formula ($SG = W_{air} / W_{air} - W_{water}$), were measured to be 1.317 g/cm^3. In fact, this unusual specific gravity value is higher from those of many organic origin coal and related blackish carbonaceous materials. The typical specific gravity of Oltu-stone is thus distinctive. Therefore, the hydrostatic balance method is a powerful tool to distinguish the Turkish carbon black material from the other natural and synthetic carbon black materials and related blackish carbonaceous materials.

3.4 X-Ray Diffraction (XRD)

Numerical data obtained from XRD analyses of the Oltu-stone samples were tried to be matched to those of ideal carbonaceous materials (diamond, graphite, nanotubes etc) compiled from the well-known database (RRUFF, 2013) and some

related publications (Brown and Altermatt, 1985) of those minerals using a comparative matching technique for XRD data.

In the XRD pattern of the Oltu-stone (Figure 3.8), a total 12 of X-ray diffraction bands are acquired. The 4.20 and 3.78 Å centred two higher bands and the 2.51, 2.28, 2.25, and 2.12 Å centred four relative lower bands are present and these are characteristic. In addition, 14.79, 3.22, 3.05, 2.72, 1.95 and 1.69 Å centred six small bands also exist in the pattern.

Accordingly, the peaks at 14.79, 4.20, 3.78, 3.22, 3.05, and 1.95 Å can be signed to carbonaceous material. The others can be signed to inclusions; the peaks at 2.51, 2.28, 2.25, and 2.12 Å regards to silica, and the peaks at 2.72 and 1.69 Å to pyrite.

Ungar et al. (2002) investigated the microstructure of synthetic carbon blacks (N990, N774, and N134) by X-ray diffraction peak profile analysis.

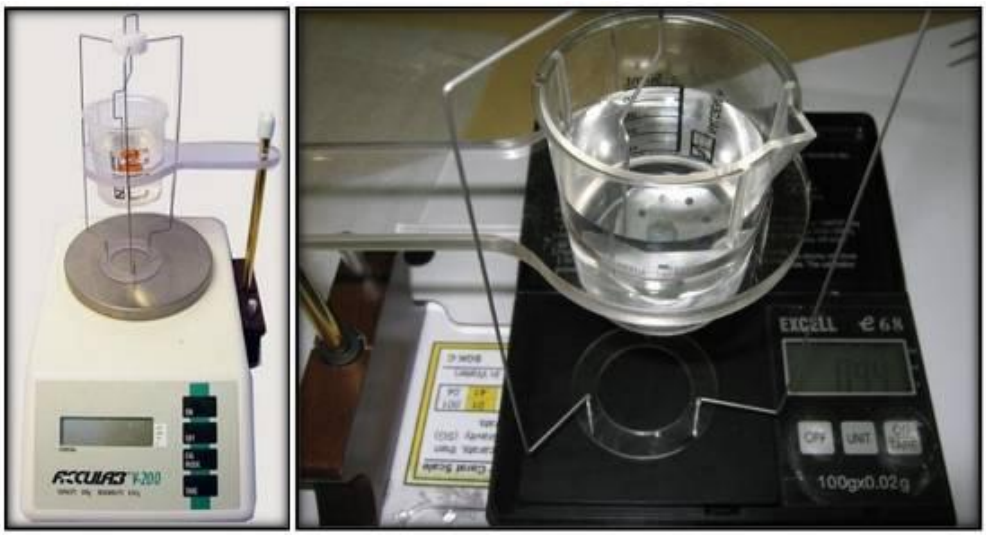

Figure 3.7 Gemmological specific gravity apparatus for sensitive measurement of the weight in air and the weight in water of Oltu-stone.

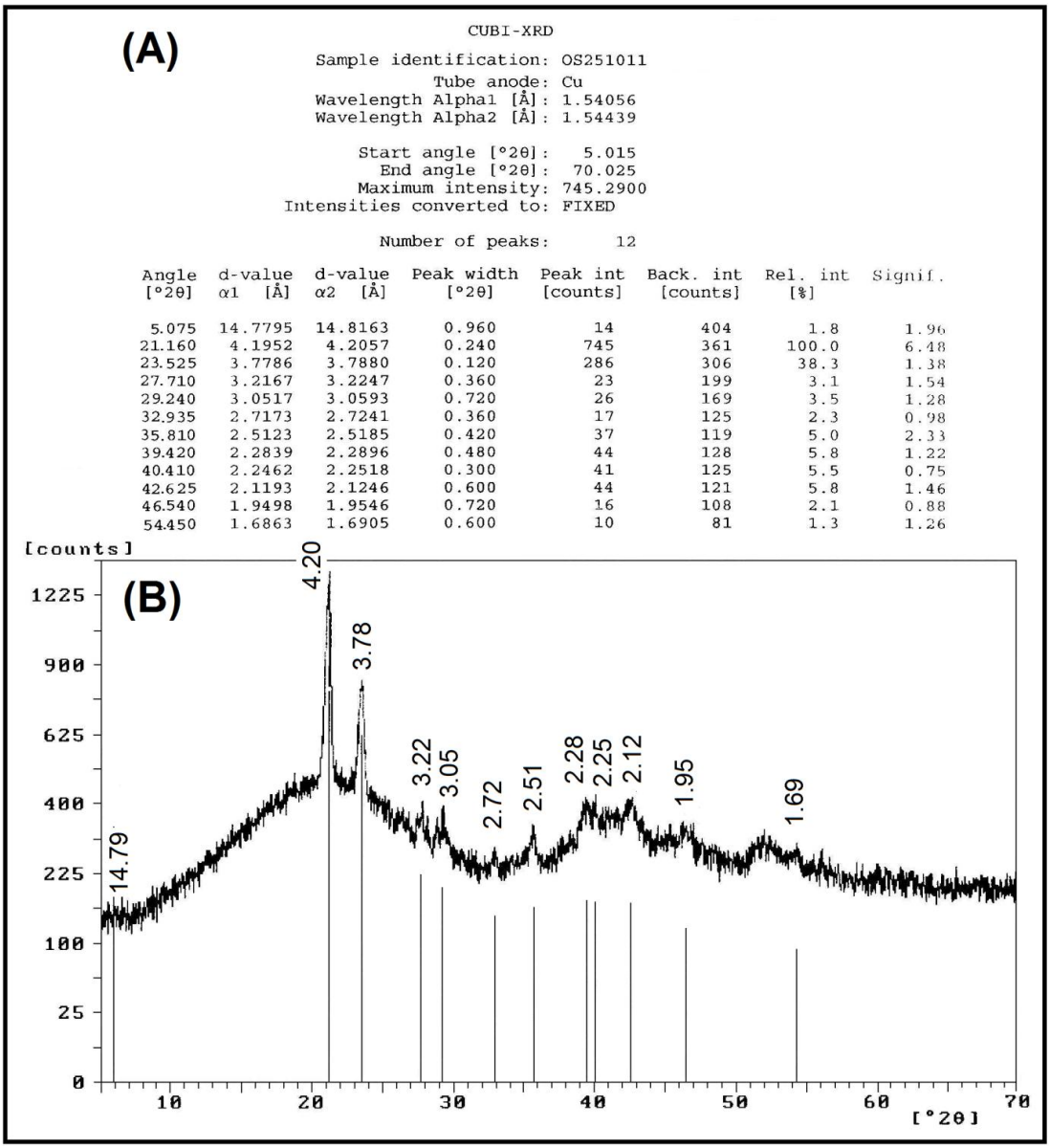

Figure 3.8 As corresponding to the numerical experimental XRD data **(A)**, the XRD pattern of a representative Oltu-stone **(B)**. The 4.20 and 3.78 Å centred two higher bands and the 2.51, 2.28, 2.25, and 2.12 Å centred four relative lower bands are characteristic.

3.5 Polarizing Microscopy

Petrographic thin-section examination under a polarized-light microscope (Figure 3.9) shows that the material cannot be considered pure graphite. Accordingly, Oltu-stone consists of mainly micro-crystallites (graphite) and amorphous carbon (soot or charcoal). In addition, Oltu-stone includes quartz and pyrite minerals. In the

chemical analysis, quartz and pyrite forming oxides are observed as 1.75% for SiO_2 and 0.50% for Fe_2O_3 as well as 0.32% for the element sulphur.

It is stated that, from the point of view of morphology and internal structure, there appears to be no difference between soot and carbon black (Lahaye et al., 1981; Clague et al., 1999). Hauptman et al. (2012) stated that X-ray photoelectron spectroscopy gives the oxygen content and the nature of functional groups on particle surfaces (Hauptman et al., 2012).

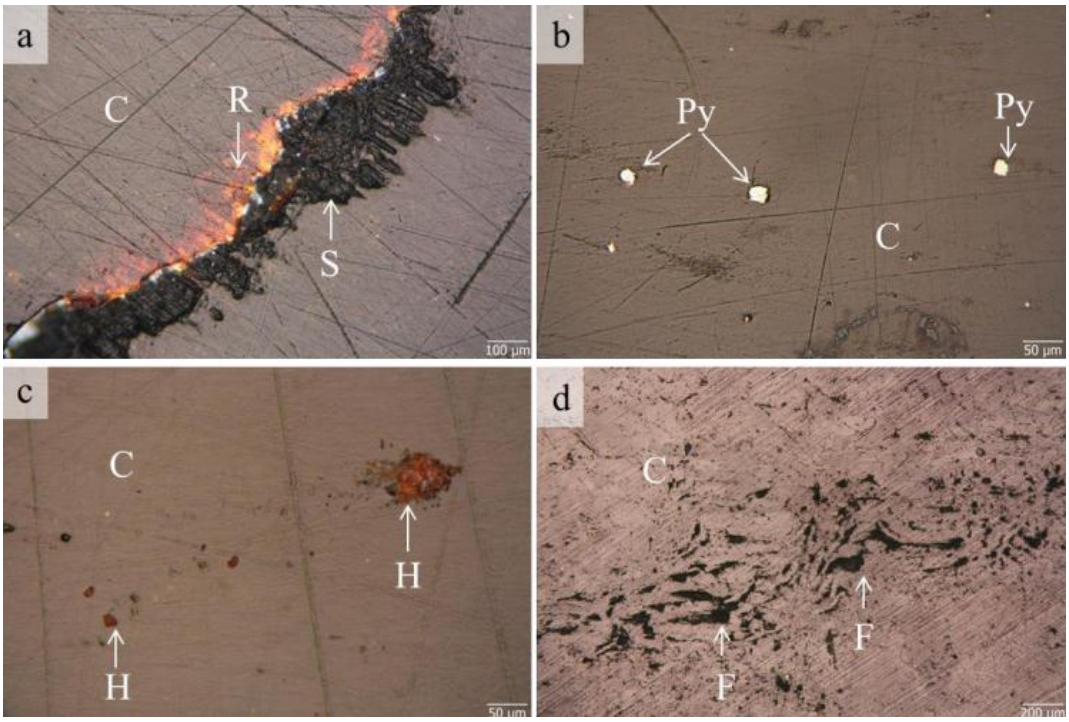

Figure 3.9 microphotographs from polished Oltu-stone samples; (a) Oltu-stone and its fracture filled with resinite and semifusinite, (b) Oltu-stone including euhedral pyrite, (c) Oltu-stone including hematite and (d) Oltu-stone including fusunite showing curved structure (C: carbone, R: resinite, S: semifusinite, H: hematite, Py: pyrite and F: fusinite).(Kalkan et al., 2012)

3.6 Scanning Electron Microscopy (SEM)

Many scanning electron microscope images (SEM) of Oltu-stone are acquired, and they are collected into the four groups (Figures 3.10, 3.11, 3.12, and 3.13).

Scanning electron micrographs of carbonaceous Oltu-stone clusters show the typical elongated habit.

The scanning electron microscope images were shown that the internal structures of the carbonaceous Oltu-stone consist of mostly low micron-sized (1.0 – 1.2 μm) and partially high nano-sized (900 – 1000 nm) carbon-building particles.

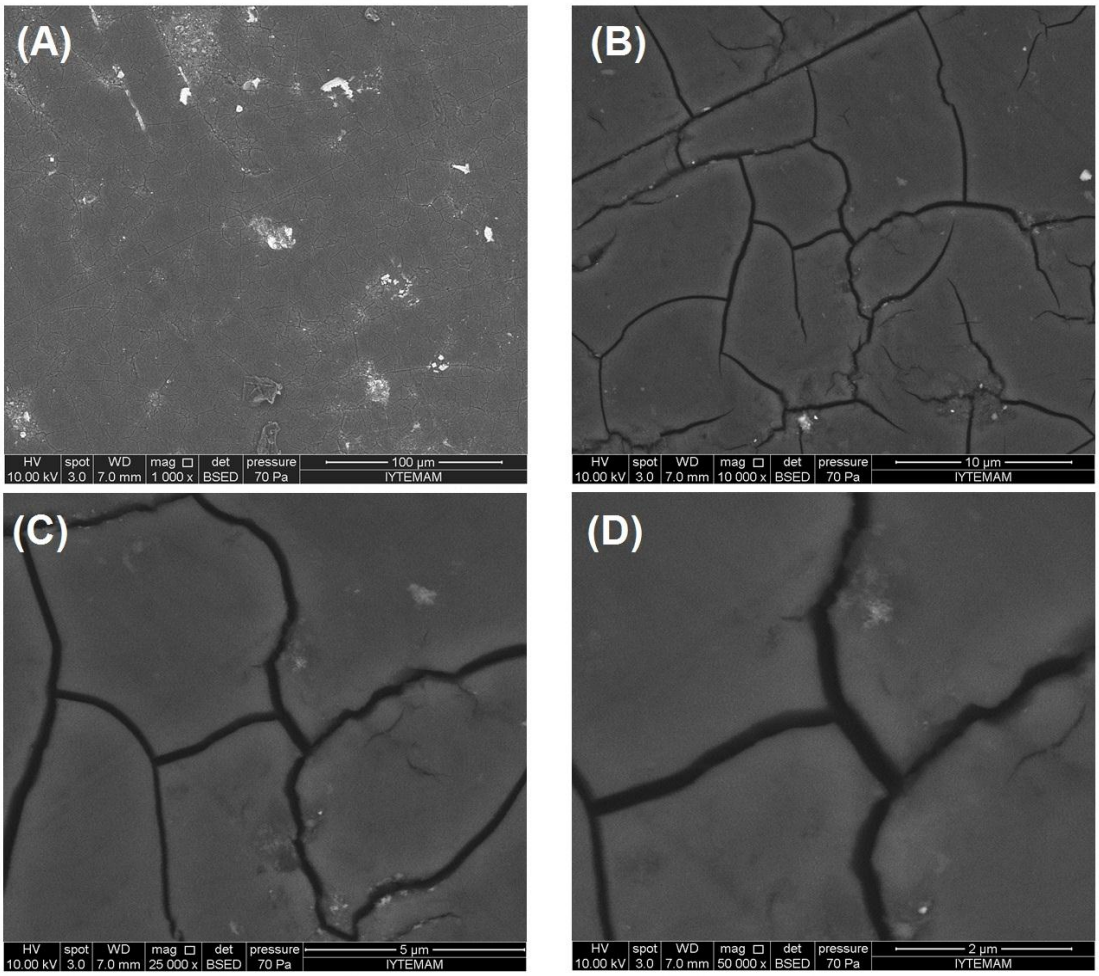

Figure 3.10 Four scanning electron microscope images (SEM) in the magnifications from 1.000x up to 50.000x of Oltu-stone obtaining with BSED only.

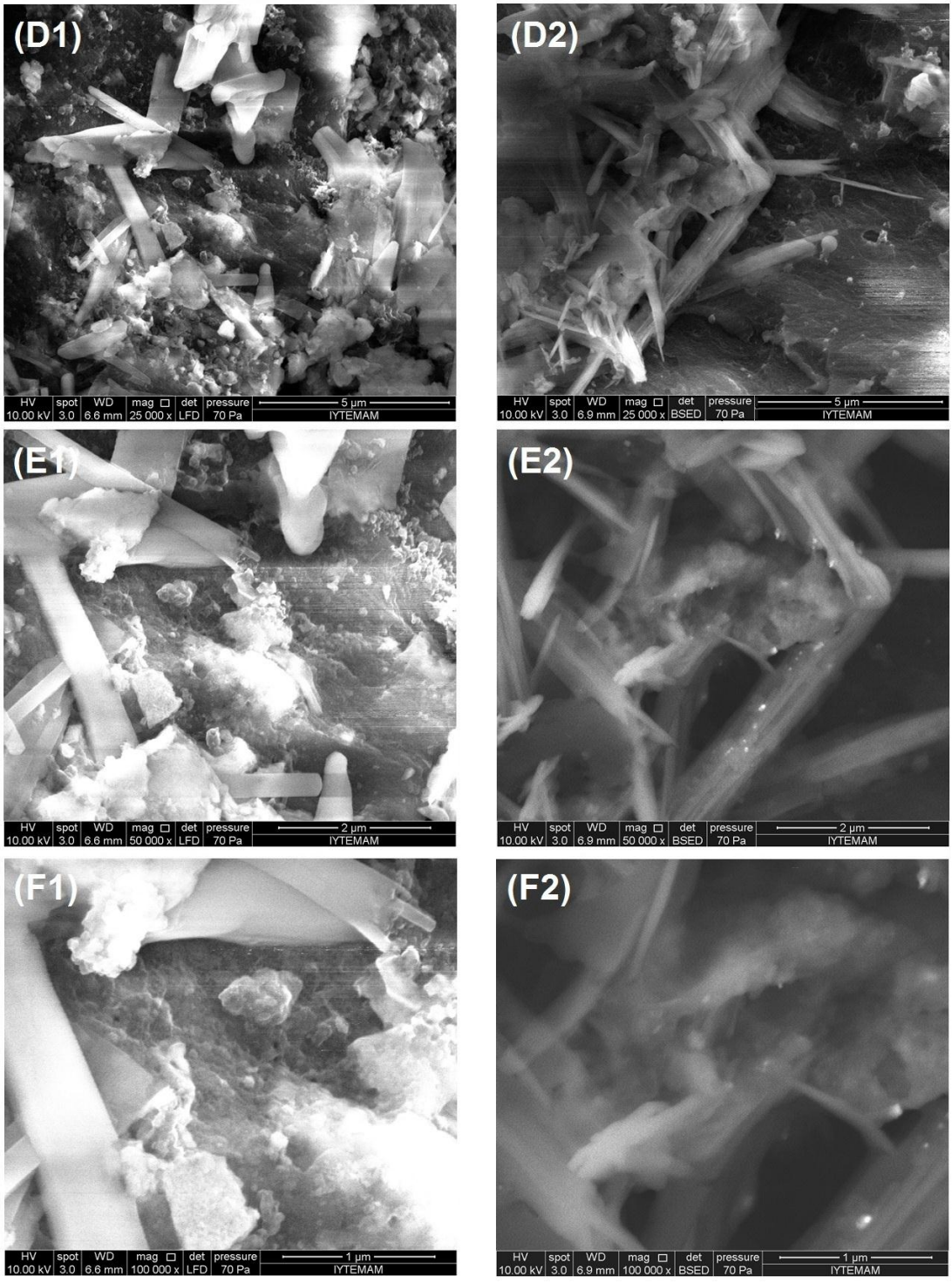

Figure 3.11 Six scanning electron microscope images (SEM) in the magnifications from 25.000x up to 100.000x of Oltu-stone obtaining with LFD (left column) and BSED (right column). Scanning electron micrographs of carbonaceous Oltu-stone clusters show the typical elongated habit.

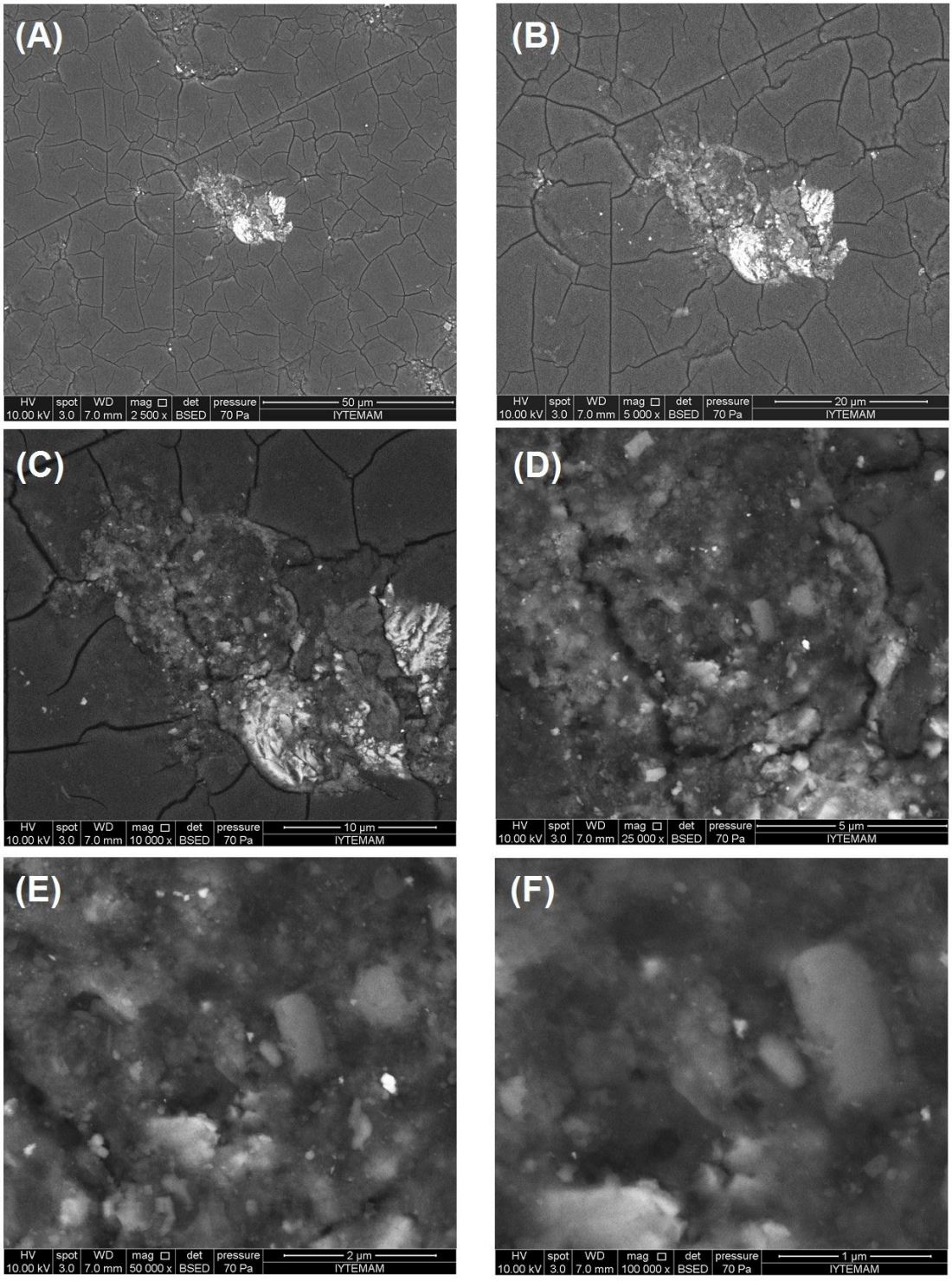

Figure 3.12 Six scanning electron microscope images (SEM) in the magnifications from 2.500x up to 100.000x of Oltu-stone obtaining with LFD (left column) and BSED (right column).

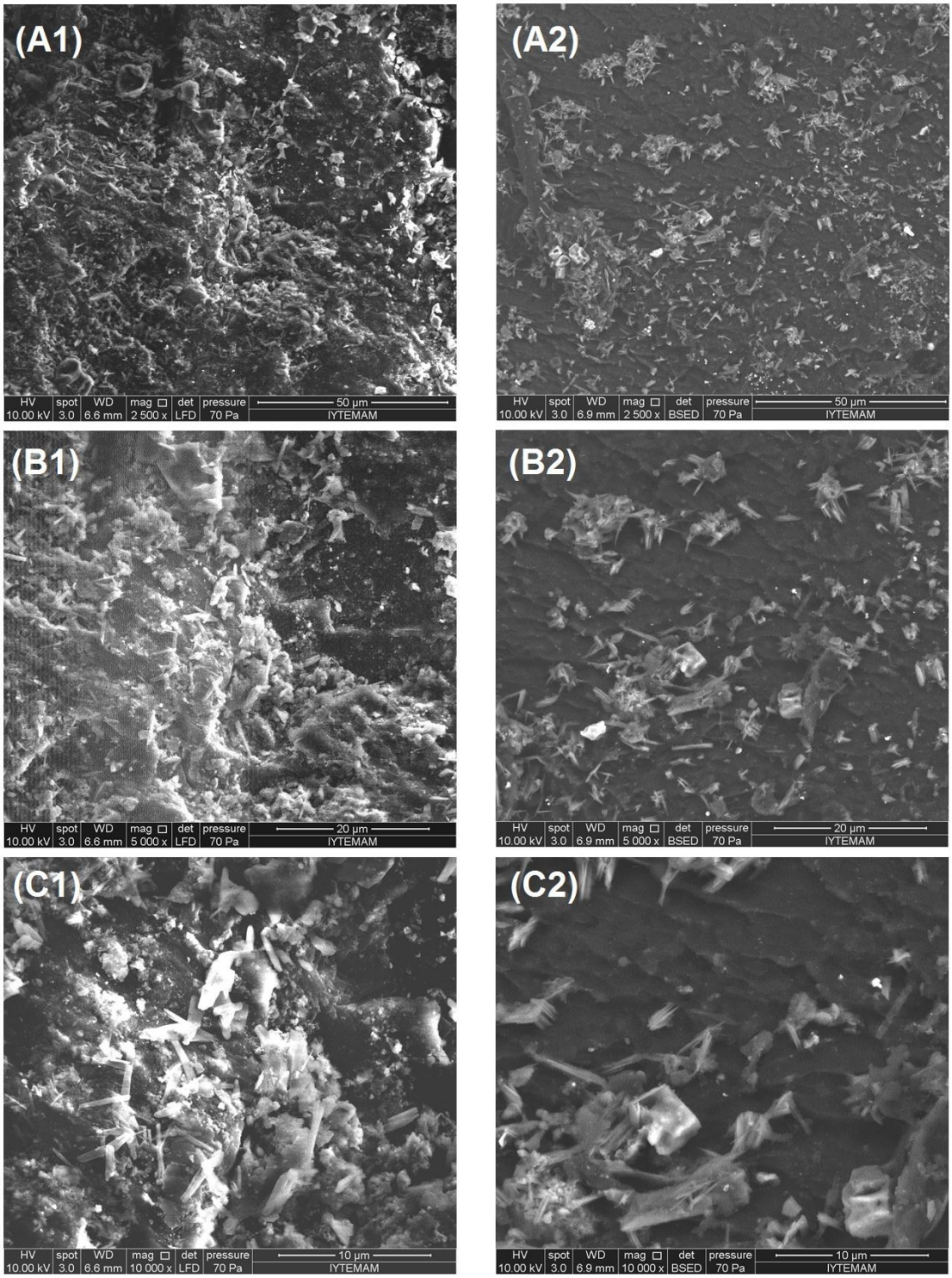

Figure 3.13 Six scanning electron microscope images (SEM) in the magnifications from 2.500x up to 10.000x of Oltu-stone obtaining with LFD (left column) and BSED (right column).

3.7 Atomic Force Microscopy (AFM)

The atomic force microscope (AFM) micrographs were taken as two different 3-D (three-dimensional) morphologies (Figure 3.14A and 3.14B) and one 2-D (two-dimensional) graphic (Figure 3.14C) for Oltu-stone. In the 3-D surface topographies, black zones show dip, and white points show high zone.

The 62.3×62.3 μm face of Oltu-stone was scanned. The topography map shows maximum and minimum level of indentation and projection. As it is seen, the grain sizes of the carbonaceous matrix have a libration with a minimum of 900 nm and a maximum of 1.2 μm.

3.8 Thermo Gravimetry (DTA/TGA)

Thermal properties and thermal stability as thermo gravimetric behaviours of Oltu-stone, including some associated mineral inclusions, were studied by thermo gravimetric analysis (TGA), and the transformations and/or decompositions of the carboniferous building blocks and/or paramorph or other inclusion minerals during the heating process can be also determined by differential thermal analysis (DTA). Accordingly, simultaneous DTA/TGA glow curves are given in Figure 3.15.

During heating to 1400 ^{o}C, the glow curves indicate that the weight loss of Oltu-stone is due to the carboniferous material loss only, and that this loss occurs in the temperature ranges between about 316.50 and 610.00 ^{o}C. In addition, after making some corrections concerning the mass gain observed, being due to the drift with buoyancy effect of the atmosphere in the TGA glow curve, Oltu-stone shows a total mass loss of 57.459% (TGA glow curve), and one distinctive sharp endotherm at 982.56 ^{o}C and three weaker endotherms (DTA glow curve). It is seen that main thermo gravimetric weight loss is about 52% at 316.5^{o}C, and the last weight loss is about 2% at 1400^{o}C. This result shows that Oltu-stone has a relatively higher resistance to over-heat

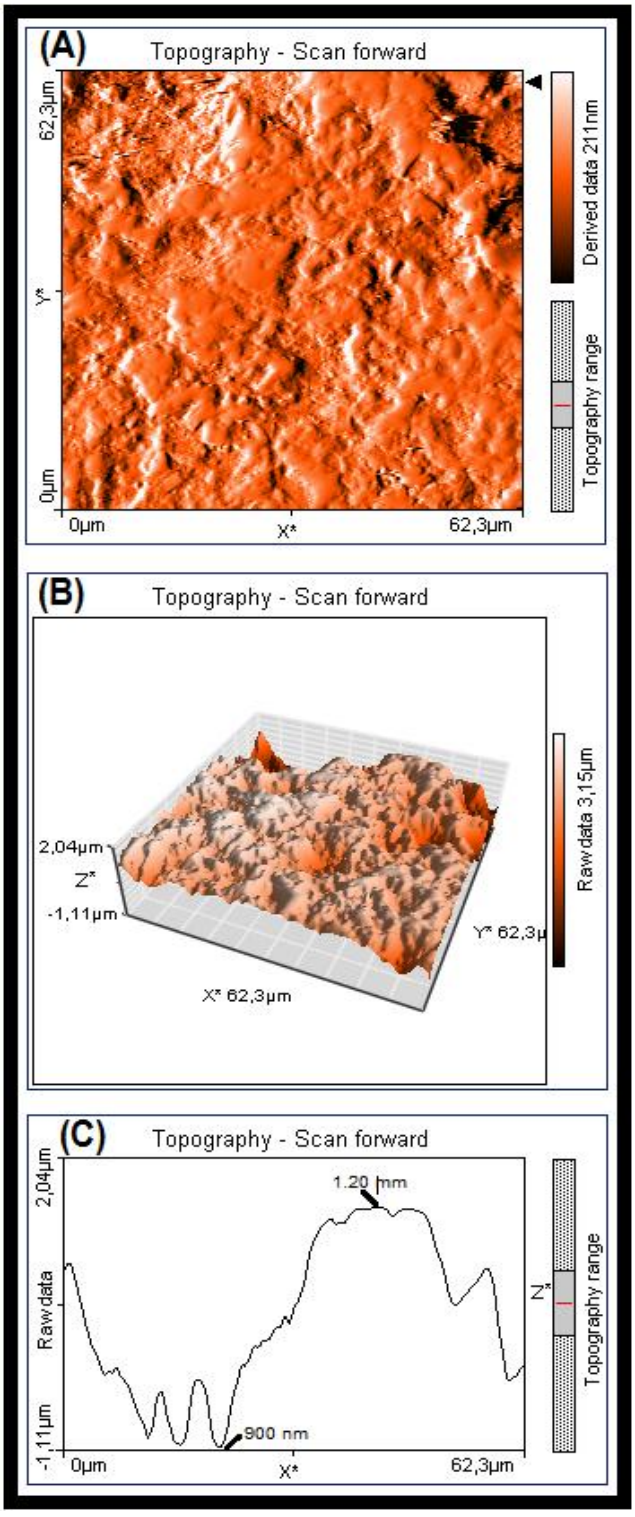

Figure 3.14 The atomic force microscope (AFM) micrographs were taken as two different 3-D (three-dimensional) morphologies **(A)** and **(B),** and one 2-D (two-dimensional) graphic **(C)** for Oltu-stone. The grain sizes of the matrix components display a libration with a minimum of 900 nm and a maximum of 1.2 µm.

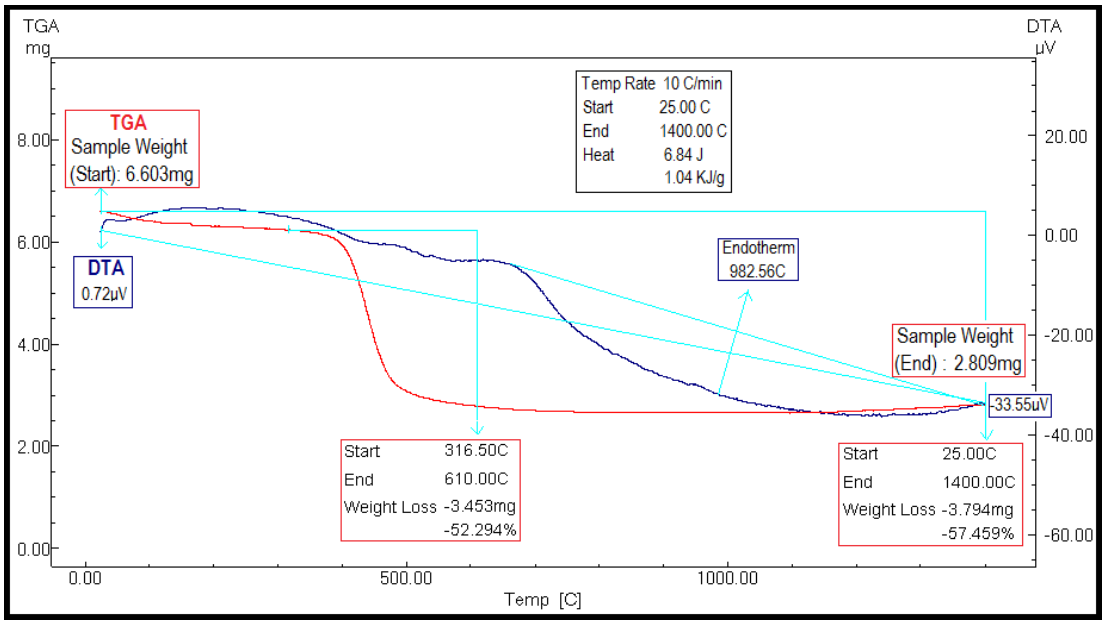

Figure 3.15 Differential thermal analysis and thermo gravimetric analysis (DTA/TGA) pattern of Oltu-stone. Acquisition measurement is simultaneously. The TGA glow curve has been corrected for buoyancy of the atmosphere. The drift observed in the dotted red lines is typical of the effect of buoyancy. Correct mass loss measurements are therefore in the straight red line, so the mass gain is an experimental artefact.

The pattern of the simultaneous differential thermal and thermal gravimetric analyses (DTA/TGA) of Oltu-stone displays slight differences compared to synthetic carbon blacks.

The thermo gravimetric (TGA) tests show that care should be taken not to exceed temperature above 316 ^{o}C in the industrial using processes. This value can also be accepted as the starting points of decomposition. The decomposition starting points of Oltu-stone seem to be slightly lower from those of the synthetic ones. However, there could be not able to find any data in the literature to contrast and compare with those of the similar natural ones found in other localities around the world. The thermo gravimetric (TGA) result can be attributed to the presence of a higher crystallinity.

The thermo gravimetric (TGA) tests show that the total mass loss per centage for Oltu-stone was found to be less than about 57%, in contrast to those of other synthetic carbon blacks (up to 65%). This may be related to silica inclusions (Table 3.1). The differential thermal (DTA) tests show that Oltu-stone is fully decomposed or transformed at about 679 ^{o}C most, probably through formation of its high temperature paramorphs. Thus, we also conclude that decompositions at the moderate temperatures are due to phase transformations entirely.

Ungar et al. (2002) have stated that heat treatment results in increased vertical and lateral sizes of graphitic crystallites. The dislocation density is increased during annealing. Concentration of amorphous carbon is decreased upon heat treatment. They interpreted this observation as a result of amorphous carbon being gradually incorporated into graphitic layers.

3.9 Micro-Raman Spectroscopy

A typical micro-Raman (532 nm green laser) spectrum (Figure 3.16), of the Oltu-stone material is given in Figure 3.17. The spectrum was recorded between 50 and 3200 cm^{-1}: measurements in a wide spectral range are evidenced, It is seen that two important peaks at 1346 cm^{-1} and 1585 cm^{-1} in the spectral range between 1000 and 1800 cm^{-1} are characteristic of the para-crystallites, other peaks can be ascribed to amorphous regions in the range between 2500 and 3000 cm^{-1}. Finally, as the main inclusions, the enhanced background between 200 and 500 cm^{-1} in these spectra may be related to SiO_2, and the higher peak at about 100 cm^{-1} could be related to Fe_2O.

The two main G bands at 1346 cm^{-1} (A_{1g}) and 1585 cm^{-1} (E_{2g}) are characteristic of the micro-crystallites (graphite) whereas the Raman peaks at 2654 and 2904 cm^{-1} are ascribed to the amorphous carbon regions on the surface. The last peaks have the "signature" of a sp^n bonded carbon. This sp^n nomenclature may represent carbon in graphitic type species highly dislocated (Brown and Altermatt, 1985). Finally, the enhanced background between 250 and 400 cm^{-1} could be associated with the presence of pyrite. We can state that micro-Raman spectroscopy investigations

indicate that Oltu-Stone (natural carbon black) crystallites are non-spherical flat discs. Similar result declared by Ungar et al (2005). In the synthetic carbon black powder samples, they were observed the strong overlap of the diffraction profiles. The overlapping peaks had to be separated since the present evaluation method was worked out for individual profiles (Ungar et al., 2005).

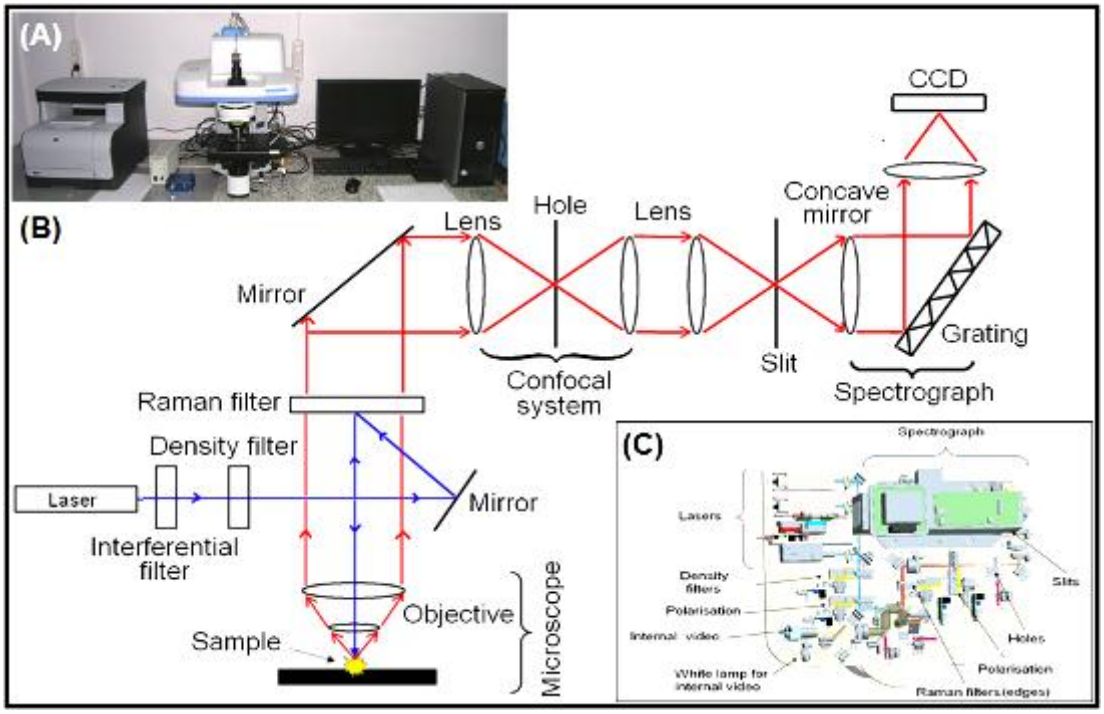

Figure 3.16 The dispersive confocal micro-Raman spectrometer in the Gemmological Testing Laboratory (DGL) of Dokuz Eylül University, used in this study **(A),** its schematic diagram **(B)** and description **(C)**.

Gruber et al. (1994) acquired Raman spectra of regular and heat-treated carbon blacks determining the changes in microstructure due to thermal treatment at five heat-treatment temperatures ranging from room temperature to 3000 K. They have stated that the peak at 1345 cm^{-1}, which was assigned to symmetric C-C vibrations, was characteristic of disordered structures and its intensity decreases with increasing

size of the graphitic planes. This band and the 1575 cm^{-1} peak characteristic of graphite had been analyzed and the ratio of their integrated intensities had used to estimate the in-plane dimensions of graphitic crystalline regions, and the size of these microcrystallites increases with temperature (Gruber et al., 1994).

As a matter of fact, in the high pressure Raman and neutron scattering study of carbon black and highly oriented pyrolytic graphite, Zerda et al. (2000) have stated that carbon black particles were composed of graphitic micro- or nano-crystallites and unknown amorphous carbon; a pressure induced frequency shift of the E_{2g} bands of various carbon blacks can be interpreted in terms of a modified intermolecular potential (Zerda et al., 2000). Hauptman et al. (2012) stated that Raman spectroscopy provides relative amounts of disordered, graphitic and amorphous phases, and the lateral size of crystallites (Hauptman et al., 2012).

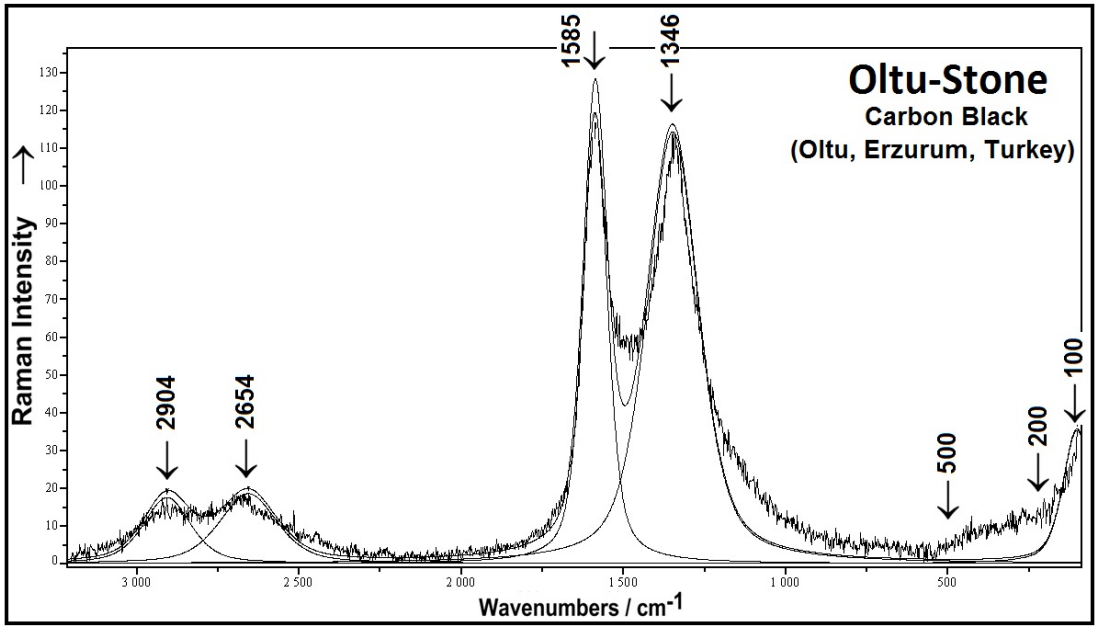

Figure 3.18 The typical spectrum of dispersive confocal micro-Raman vibrational bands of the Oltu-stone material. Two important peaks at 1346 cm^{-1} and 1585 cm^{-1} in the spectral range between 1000 and 1800 cm^{-1} are characteristic of the quasi-crystallites, other features ascribed to amorphous regions in the range between 2500 and 3000 cm^{-1}, and finally, as the main inclusions, the enhanced background between 200 and 500 cm^{-1} in these spectra could be related to SiO_2, and the higher peak at about 100 cm^{-1} could be related to Fe_2O (modified from Hatipoğlu et al.,2012)

The synthetic carbon sample obtained from the pyrolysis of GC-MASS (LIN, 2002) exhibits a Raman pattern similar to that of natural carbon black. Similar Raman results were reported in previous papers (Wang et al., 1994; Jawhari et al., 1995; Zerda et al., 2000) and in a mineral database (RRUFF, 2013), while original graphite exhibits a bit different spectrum (Tuinstra and Koening, 1970). Ungar et al. (2002) have stated that Raman measurements in synthetic carbon blacks indicated smaller crystallites than those measured by X-rays because the Raman spectra were mainly due to the outer skin of the aggregates while X-ray diffraction detects crytallites throughout the volume (Ungar et al., 2002).

When it is compared and contrasted the dispersive confocal micro-Raman spectra (Figures 3.18, 3.19, and 3.20) of all kind of carbon materials including Oltu stone, it is seen that the spectra of two different Oltu stone materials match to carbon-black spectrum. It is seen that the spectrometer is very suitable method to distinguish and identify non-destructively and non-invasively the all kind of carbon materials as well as cheapest method. This aspect is very attractive for the researchers who are working on carbon materials (Figure 3.21).

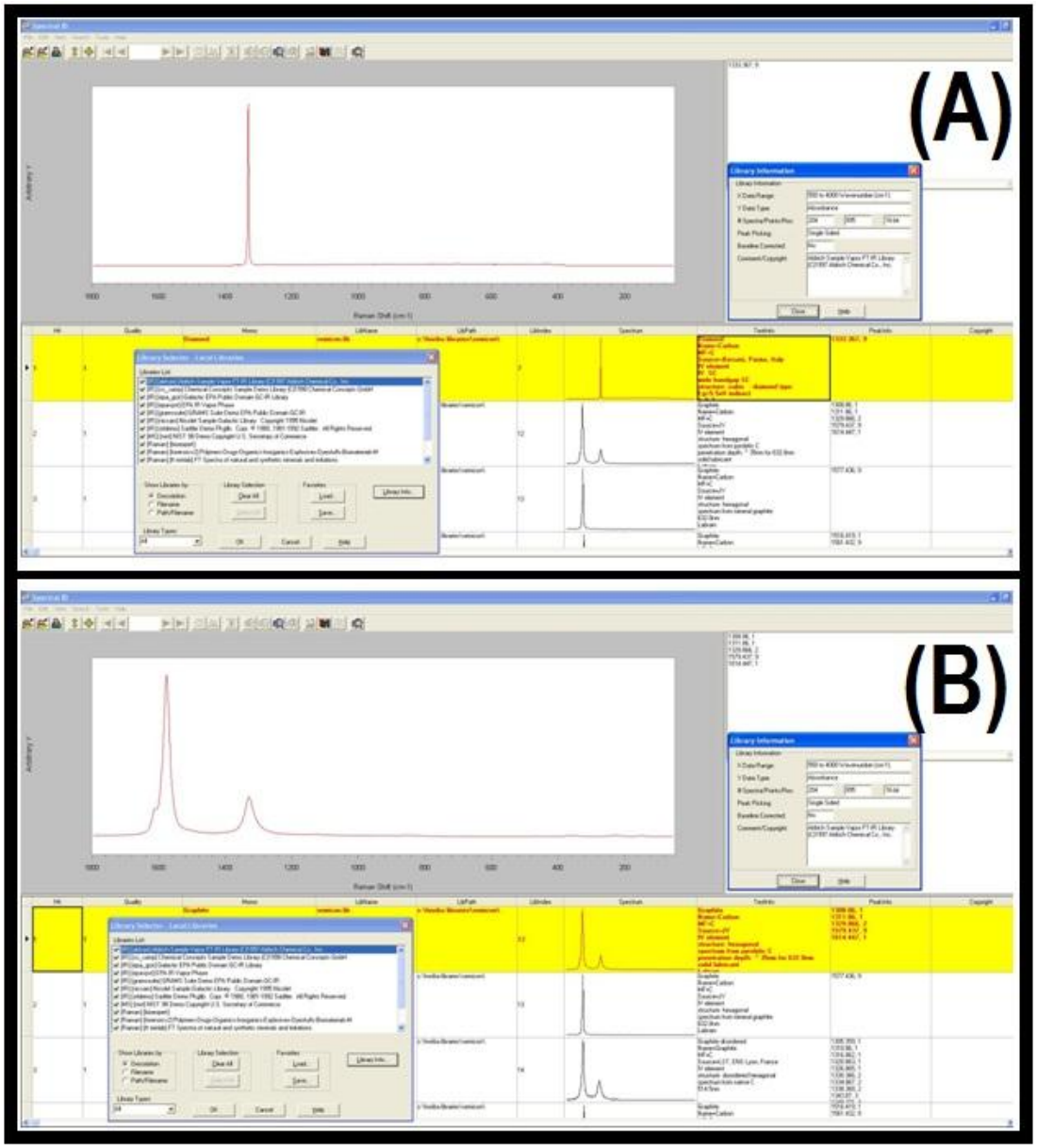

Figure 3.18 Compare and contrast graphics of diamond **(A)** and graphite **(B)**.

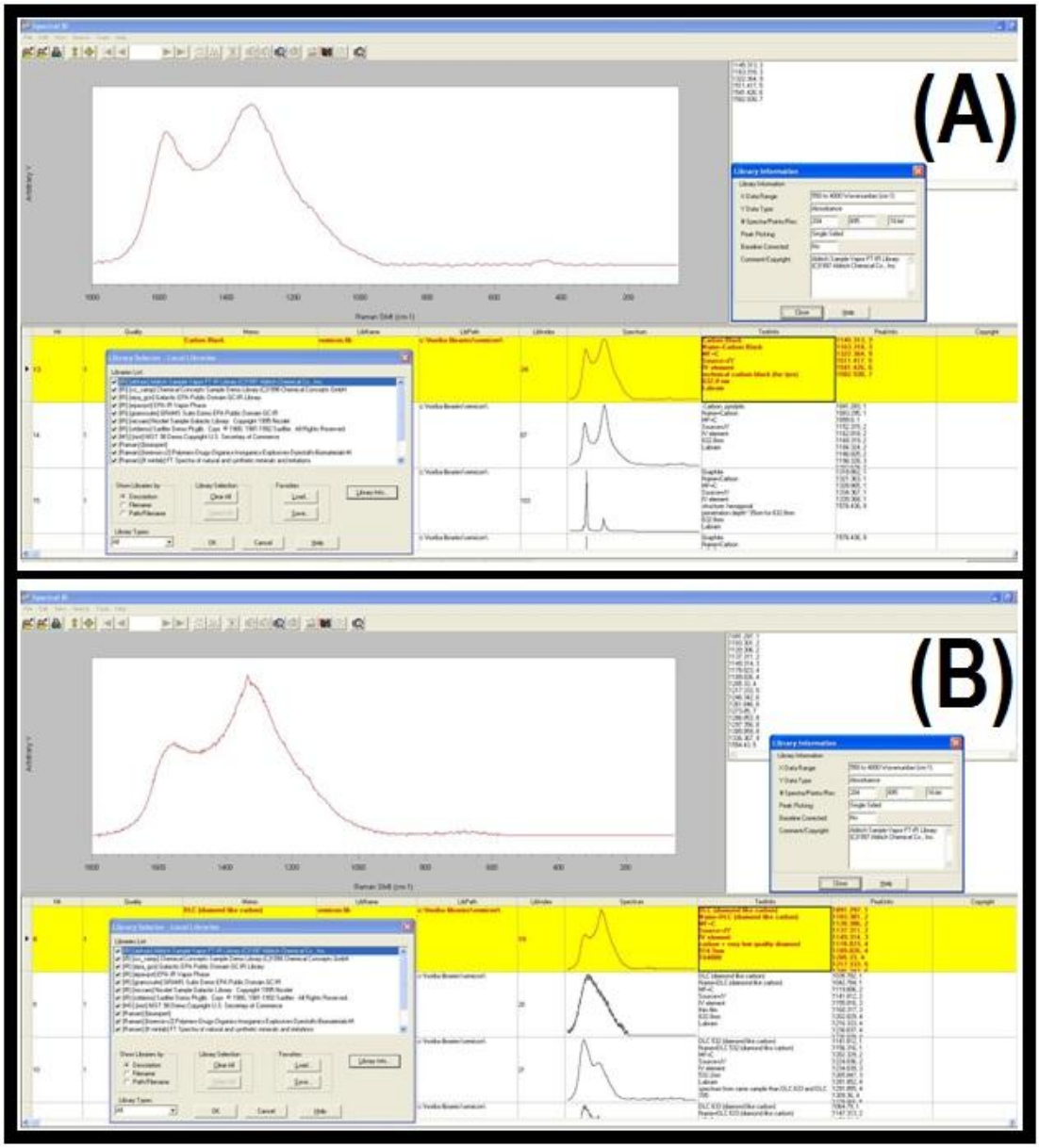

Figure 3.19 Compare and contrast graphics of carbon black **(A)** and diamond-like carbon **(B)**.

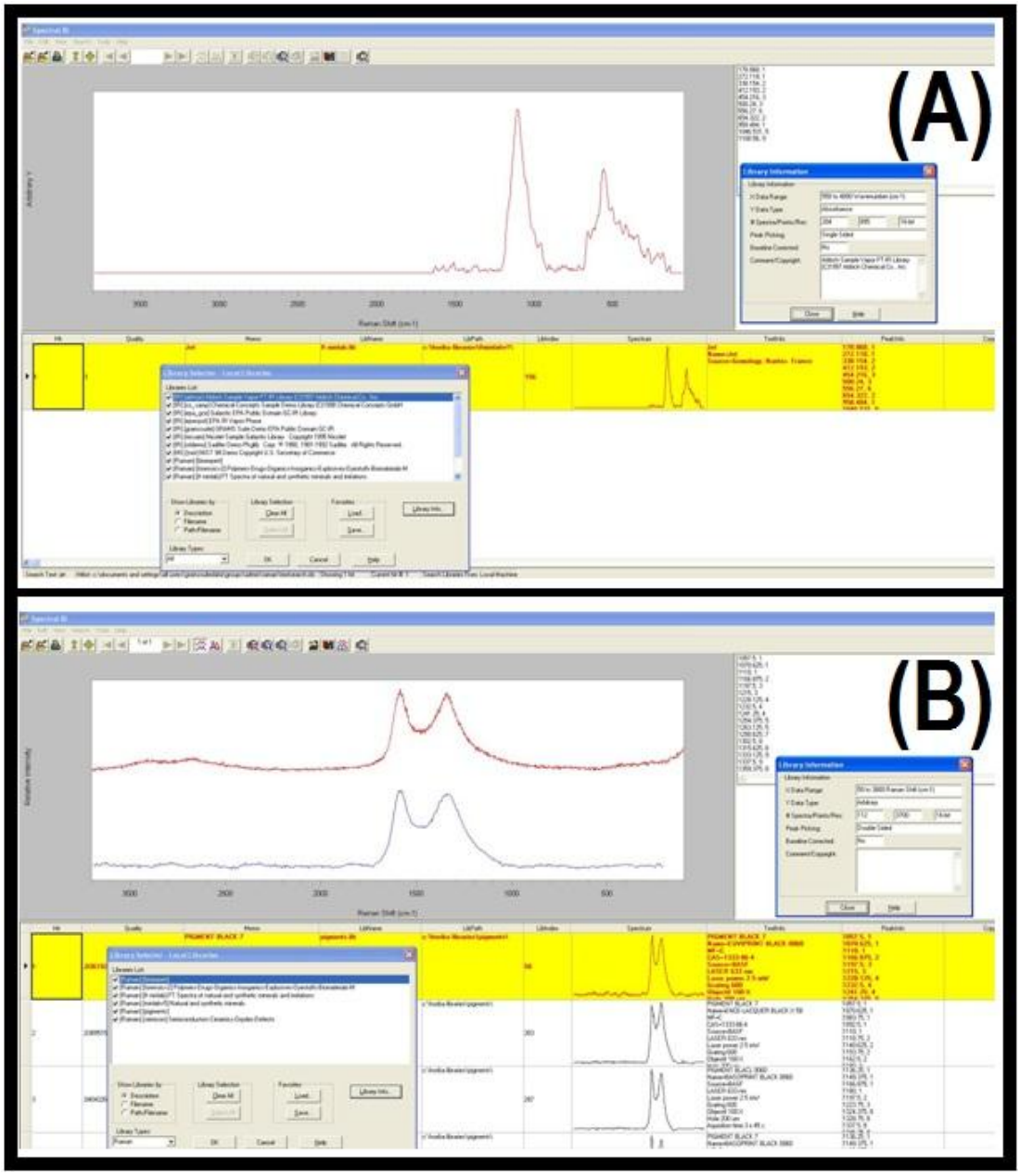

Figure 3.20 Compare and contrast graphics of jet **(A)** and Oltu-stone **(B)**.

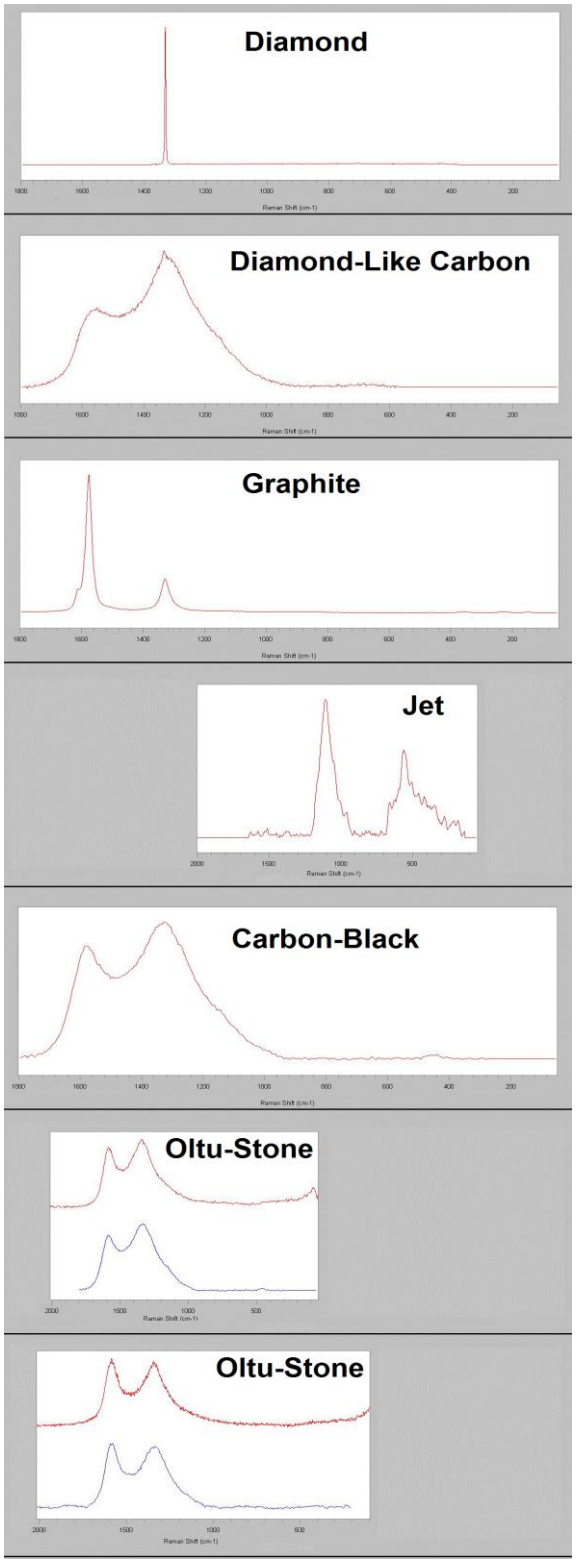

Figure 3.21 The dispersive confocal micro-Raman spectra of all kind of carbon materials including Oltu-stone for comparison and contrast. All spectra are obtained from the same spectrometer.

CHAPTER FOUR
CONCLUSIONS

A great deal of attention has been given in the last thirty years to the modelling approach of natural carbon black formation. Chemical analyses, specific gravity measurements, X-ray diffraction patterns, polarizing microscope studies, scanning electron images, atomic force microscope evaluations, thermo gravimetric glow curves, and confocal micro-Raman bands were performed to identify the homogenous carbonaceous material of the Oltu-stone relating to its physical and mineralogical characteristics for genesis.

The formation of Oltu-stone can be considered to incorporate many of the features common to the thermal oxidative decomposition processes. We can state that this is a material composed essentially of elemental carbon in the form of tabular particles.

The remarkable abundance of main radioactive elements, such as Sr (10.5 ppm), Th (0.38 ppm), U (023 ppm), and Zr (67 ppm), can be attributed to inorganic material genesis for Oltu-stone, instead of organic material genesis.

This image can be generally attributed to crystallite-rich carbon black structure as well as amorphous-rich jet-coal and/or the other diamond-like carbons. However, ratio of the chemical content and mainly micro-Raman spectra of the Oltu-stone can allow us identify as carbon black. The results of the Raman analyses are in good agreement with the data obtained from X-ray diffraction. Raman spectroscopy investigations indicate that Oltu-Stone (natural carbon black) crystallites are non-spherical flat discs.

The measurements of these all kind of analytical parameters are the most trustworthy method to distinguish the natural Turkish carbon black from the other well-known kinds of natural and synthetic, carbon black materials. In addition, these

parameters provide positive identification of the provenance (geographic origin) of the original Oltu-stone.

Oltu-stone gets demands from processors and consumers in Turkey gemstone market because of not only its abundant application areas but also its workability. However, the most aggrieved people in oltu-stone trade are oltu-stone collectors who works in the mines. They do this work in non-modern conditions and in great danger for a long time. Although they work under great danger, their earnings are very low. Price of an oltu-stone beads varies between 100 and 500 tl. However, oltu-stone collectors gets the minimum earnings. The price of oltu-stone sold with tin account varies between 2000 and 3000 tl according to its characteristics. Approximately 200 pieces of oltu-stone object can be obtained from a tin of oltu-stone.

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