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Gemological – geochemical characteristics of western Anatolian (Karacasu) citrines

Introduction

Natural stones have taken part in daily life as cutting-drilling functions and agricultural tools almost since the beginning of humanity, and their usage areas have expanded in parallel with the progress of humanity. Humans have used natural stone in many areas, from religious rituals to communication tools, from dye production to stone structures (Taslıgil and Sahin 2016; Horasan and Ozturk 2021; Horasan et al. 2022).

Ornamental stones are considered one of human history's most valuable objects. Traces of this can be seen in all social communities around the world. Even in prehistoric times, ornamental stones were loaded with meaning and were indicators of the beauty, power, and status of the person they carried (Schumann 2009).

Even thousands of years before the science of geology, people searched for and valued gemstones (Stern et al. 2013; Kınacı et al. 2023). Ornamental stones are formed by elements such as oxygen, carbon, aluminum, silicon, calcium, and magnesium, which are commonly found in nature (Vieil et al. 2004).

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The most prevalent group of gemstones worldwide is the silica group. Gemstones in the silica group have the chemical formula SiO_2. The primary reason for the color differences among members of this group is the presence of trace amounts of various elements (such as Fe, Ni, Cr, and Cu) in their chemical composition (Götze et al. 2001, 2004; Caucia et al. 2016; Başıbüyük 2018; Akbudak et al.2018; Başıbüyük et al. 2023).

Quartz is a semi-precious inorganic gemstone composed of Silicon dioxide (SiO_2). Naturally, the quartz structure is crystallized in the trigonal system in the single mineral group, which commonly has a prismatic crystal habit (Klein and Dutrow 2008; Monarumit et al. 2021). Quartz is the most important silica polymorph in nature and occurs as a common component of igneous, metamorphic, and sedimentary rocks. The mineralogy and mineral chemistry of quartz are determined primarily by its defective structure. Under different thermodynamic conditions, quartz can include specific point defects, dislocations, planar defects, and microfluid/melt and mineral inclusions during crystallization. Additionally, secondary processes including alteration, irradiation, diagenesis, or metamorphism, can also incorporate quartz (Götze et al. 2004).

Point defects in quartz may be associated with silicon or oxygen vacancies (intrinsic defects), different types of displaced atoms, and/or the incorporation of foreign ions into lattice sites and interstitial positions (extrinsic defects). Due to the mismatch in charges and ionic radii, only a limited number of ions can replace Si^{4+} in the crystal lattice or be incorporated into intermediate positions (Götze et al. 2021).

Quartz without impurities is colorless but can be found in various colors caused by some trace elements such as amethyst (purple quartz), citrine (yellow quartz), rose quartz (pink quartz), etc. Citrine can be found more easily in nature than other precious stones (topaz, ruby, tourmaline). When processed, it appears in a wide variety of shades of yellow (from sunny yellow to earthy), which adds to its appeal.

Most of the contaminant elements in quartz are present in concentrations below 1 ppm. It was determined that Al^{3+}, Ga^{3+}, Fe^{3+}, B^{3+}, Ge^{4+}, Ti^{4+}, P^{5+} and H^{+} participate in structural unification in a regular Si^{4+} lattice region (Götze et al. 2021). In the few studies conducted on citrine, Weil (1984) reported that the impurity causing the yellow color was iron, Nassau (1981) reported that silica was replaced by iron, Jenkins and Larsen (2004) reported that trivalent iron caused the yellow color and Ertik (2013) reported that the source of the yellow color was iron. Ertik (2013) stated that it is hematite (Fe_2O_3) or limonite ($FeO(OH).nH_2O$). Today, quartz is one of the important gemstones in the colored stone trade.

There are many mineralogical formation regions in Turkiye with high quality gemological features and precious stone features (Ethem 2007; Yıldız et al. 2023). There is no existing scientific study on the presence of citrine, its geological, geochemical, and gemological characteristics in Turkiye. Therefore, this study is considered the first and only research conducted on citrine in the region and the country, contributing to the scientific literature and serving as a reference for future studies.

In this context, the aim was to investigate the geological, geochemical, and gemological properties of citrine formations in the Western Anatolia (Karacasu) region and to determine the gemstone quality.

1. Materials and methods

This study was conducted to determine the geology and gemological features of the area where citrines are found. Studies were carried out in three stages to investigate citrines. In the first stage, the geology of the study area was evaluated and boundary relations in the formations where citrines were found were investigated. Samples were collected from the regions within the study area. In the second stage of the study, analyses were carried out to determine the chemical and gemological properties of the samples.

Chemical analyses were carried out using XRF and Raman Spectrometry in Necmettin Erbakan University BITAM laboratories. For XRF analysis, the samples were ground in a ring mill to a size below 10 μm. The samples, which were reduced to a size below 10 μm, were analyzed with the Rigaku – NEX-CG brand XRF device, and the amount of elements and oxides contained were determined.

The Raman spectrum was obtained with the Renishaw Invia reflex confocal Raman microscope with 532 nm laser, 1,800 l/mm grating, 20× objective, 10 sec exposure time, 125–2,000 cm^{-1} range, 10 acquisition operating conditions.

Since gemstone samples are rare and economically important, non-destructive analysis methods are preferred in gemology. Therefore, measurements are made while the sample is raw or polished. A single 16.61 g cabochon sample was used for Fourier Transform Infrared Spectroscopy (FTIR) measurement and the photo of the sample was added to the FTIR chart. For this purpose, scans were obtained with the MAGILABS GemmoFtir™ spectrometer equipped with a low-noise DLATGS- detector and Fourier Transform Infrared Spectroscopy (FTIR) at a resolution of 4 cm^{-1} for a measurement time of 20 seconds. With this method, peaks were formed by detecting the characteristic fingerprint of the samples, which were used for chemical identification. The FTIR analysis process was carried out in the General Directorate of Mineral Research and Exploration (MTA) – Ankara Central Laboratory.

Its gemological properties were examined in the MTA – Ankara Central Laboratory and Batman University Jewelry and Jewelry Design Department laboratories. In the third stage, the samples taken were faceted and shaped.

2. Results

2.1. Geological setting

The Menderes Massif, in which the study area is located, is divided into two: the core and the overlying cover series (Schuiling 1962; Dürr 1975; Dora et al. 1990). It is stated that it is divided into 3 parts: the Northern, Central, and Southern (Çine) as submassive. It has been stated that the boundaries of these submissives are formed by the E-W trending Gediz Graben in the north and the Big Menderes Graben in the south (Bozkurt 2001). Accordingly, the core part of the massif consists of high-grade metamorphics such as Precambrian-Cambrian aged granitic gneiss, augen gneiss, banded gneiss, and migmatite gneiss. The basal relationships of these gneisses, whose apparent thickness reaches 2–3 km, cannot be seen. The core rocks are covered by an Ordovician-Paleocene aged cover series consisting of lower-grade schists and marbles (Dora et al. 1990).

Important albite (feldspar) and quartz deposits in the Çine Submassif are more common, especially in the southern parts of the core, and are primary pegmatitic formations located

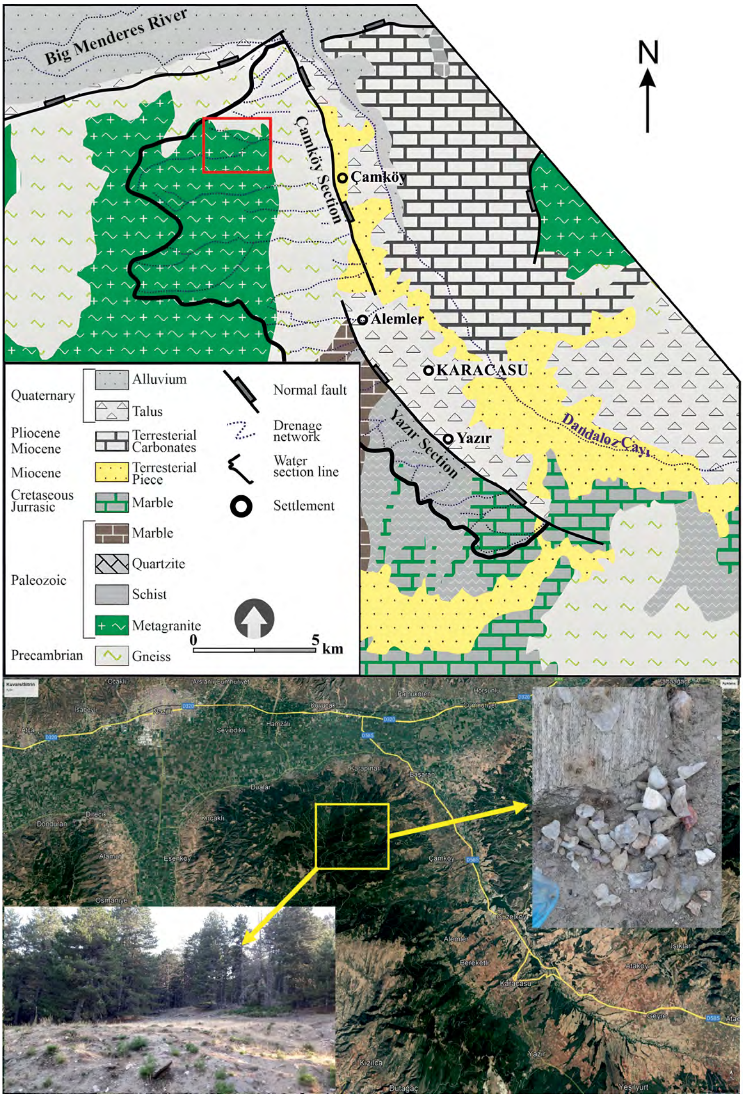

Fig. 1. Study area geolocation and geological map
(Topal 2019; Konak and Goktas 2001; Acıkalın 2005; Alcicek and Jiménez-Moreno 2013)

Rys. 1. Geolokalizacja obszaru badań i mapa geologiczna within NNE-trending tectonic lines. Tourmaline, K-Feldspar, and quartz veins in the region are of hydrothermal origin (Uygun and Gumuscu 2000; Gül 2018).

Kastelli (1971), where the geological investigation of the Karacasu region was carried out, it was stated that Early Pliocene-aged units came over the metamorphic rocks after a large time gap and this series was unconformably overlain by Upper Pliocene sediments. It has been stated that Quaternary sediments consist of terraces, old and new alluviums, fans, and accumulation cones (Figure 1).

Citrines, which are the research subject of this study, are located in a very limited and narrow area (approximately 40–50 cm) in the form of thin veins in the contacts of the metamorphic units and limestones in the region and the crack zones of the metamorphic units.

2.2. XRF

In the chemical analysis of the samples taken, the SiO_2 ratio was 85% wt. and the Fe_2O_3 ratio was 0.0574–0.0789% wt. (Table 1, 2).

Table 1. Trace elements (ppm)

Tabela 1. Pierwiastki śladowe (ppm)

	Detection Limit	Ct-1	Ct-2
Al	0.0128	0.313	0.201
Si	0.0726	39.5	40.1
S	0.0003	0.0029	0.0021
Cl	0.0002	0.005	0.005
K	0.002	0.0126	0.015
Ca	0.0014	0.0167	0.0095
Ti	0.0005	0.0039	0.0025
V	0.0003	0.0001	0.0001
Cr	0.0002	0.0009	0.0005
Mn	0.0008	0.002	0.002
Fe	0.0005	0.0396	0.0624
Cu	0.0002	0.0008	0.0005
Zn	0.0002	0.0003	0.0001
As	0.0001	0.0001	0.0001
Sn	0.0003	0.0014	0.0015
Pb	0.0002	0.0002	0.0001
Bi	0.0001	0.0004	0.0001
Zr	0.0003	0.15	0.05

Table 2. Chemical analysis results of main oxide elements (% wt.)

Tabela 2. Wyniki analizy chemicznej głównych pierwiastków tlenkowych (% wag.)

	Detection Limit	Ct-1	Ct-2
SiO_2	0.1580	86	87
Al_2O_3	0.0247	0.6	0.49
ZrO_2	0.0004	0.2	0.15
Fe_2O_3	0.0007	0.057	0.078
CaO	0.0020	0.023	0.012
K_2O	0.0024	0.015	0.012
SO_3	0.0006	0.007	0.006
TiO_2	0.0008	0.006	0.004
MnO	0.0011	0.002	0.001
SnO_2	0.0004	0.001	0.001
Cr_2O_3	0.0003	0.001	0.0008
CuO	0.0002	0.001	0.001
ZnO	0.0002	0.0004	0.0004
PbO	0.0002	0.0002	0.0002
As_2O_3	0.0001	0.0001	0.0001

2.3. Raman spectrometer

The application of micro-Raman has proven to be a successful non-destructive technique for investigating gemstones (Jeršek and Kramar 2014). Additionally, micro-Raman can help us identify inclusions that can reveal the origin of gemstones (Jeršek and Kramar 2014). Ten acquisition Raman spectrometry analyses were performed on citrine samples and this analysis confirmed the identity of the material as citrine.

As a result of Raman spectrometry analyses on citrine samples, Karacasu citrine was found to be 175 cm^{-1}, 300 cm^{-1}, and 460 cm^{-1} (Figure 2).

2.4. FTIR

When it comes to differentiating gemstone variations of the same mineral, FTIR may have certain limits. Figure 3 shows a nearly perfect overlap of the reflectance spectra

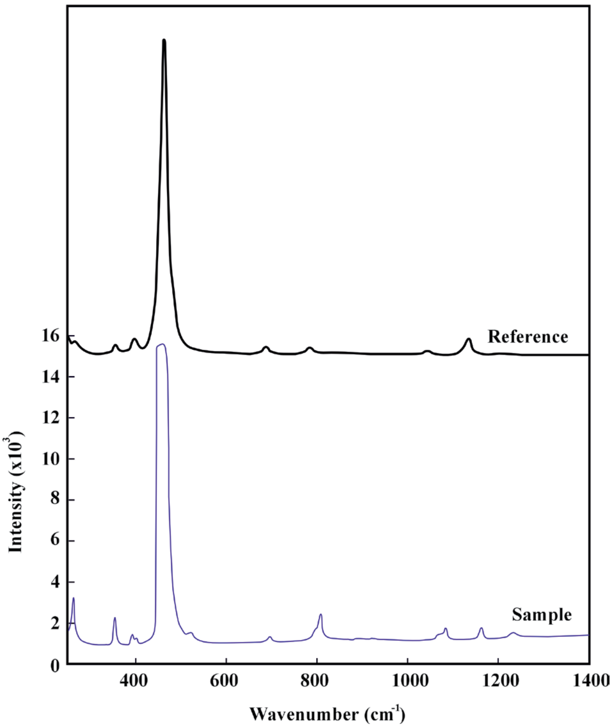

Fig. 2. Raman spectrometry of Karacasu citrines (blue line) and citrine found in the rruff da-tabase (black line) (X080016) (Jeršek and Kramar 2014)

Rys. 2. Spektrometria ramanowska cytrynów z Karacasu (niebieska linia) i cytrynu znalezionego w bazie danych RRUFF (czarna linia) (X080016)

of citrine chosen based on the various sources of color: color centers (amethyst), pseudo-chromatic coloration due to physical optic effects (venturine), and allochromia caused by transition metal impurities (citrine, rose quartz, vermarine). Since two of the most macroscopically obvious physical characteristics of minerals are their color and state of aggregation, this restriction may not be a problem for identifying these geomaterials (Izzo et al. 2020).

Because of weak derivative-like distortion (Izzo et al. 2020), the quartz FTIR spectra recorded perpendicular to the c-axis preserve the regular diagnostic doublet at ~800 cm^{-1} and ~780 cm^{-1} (Si-O bending and Si-O-Si stretching vibrations), which are generally shifted toward a higher wavenumber than the traditional IR spectra (Mercurio et al. 2017).

The result of FTIR analysis on the sample (red line) was compared with both the library of the device (black line) and the study of Izzo et al. (2020) (blue line), and the consistency of the obtained data suggests that the sample is citrine (Figure 3).

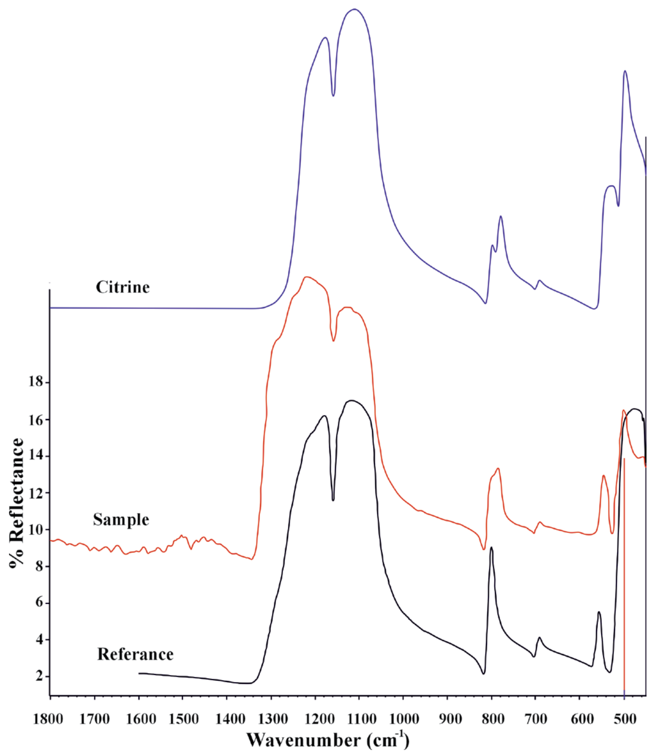

Fig. 3. Black line reference peak, Red line FTIR spectra of citrine sample,
Blue line FTIR spectra of citrine from (Izzo et al. 2020)

Rys. 3. Czarna linia piku odniesienia, czerwona linia widma FTIR próbki cytrynu,
niebieska linia widma FTIR cytrynu z

2.5. Gemological characteristics

Citrine, a yellow-colored quartz derivative, is one of the gemstones that attracts attention with its specific optical and physical properties (Figure 2, 3). The collected samples were subjected to shaping. While the transparent, crack-free, and color-integrated parts were faceted, the more opaque and cracked parts, compared to other parts were processed as cabochons (Figure 4). The dimensions of the faceted citrine are 25 carats 22 × 16 × 9 mm, while the cabochon piece is 16.61 grams and its density is 2.64 grams/cm^3.

3. Discussion

Quartz veins found in metamorphic rocks attract attention with their yellow color tones in some regions. This was investigated especially for ornamental stones and its geo-chemical

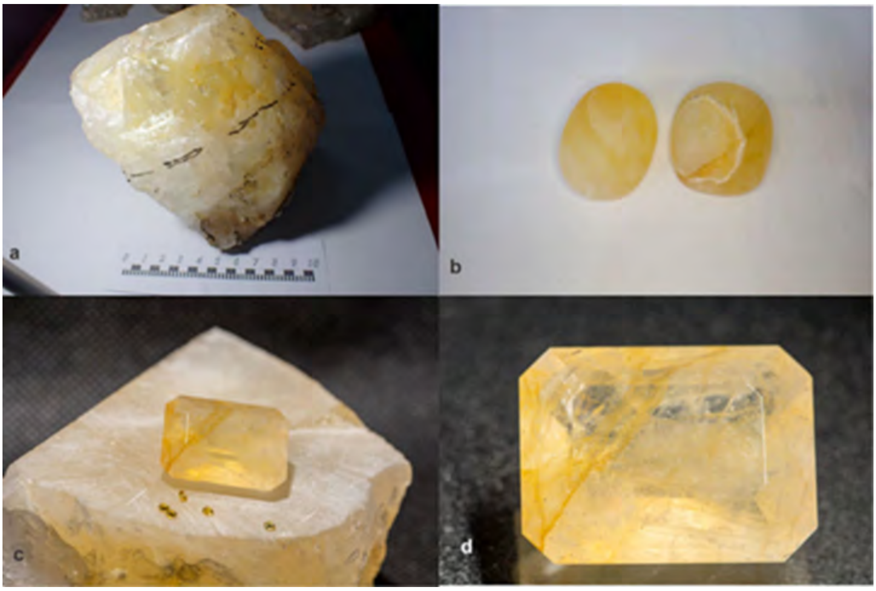

Fig. 4. a. Natural state; b. Cabochon view; c–d. View after faceting

Rys. 4. a. Stan naturalny; b. Widok kaboszonu; c–d. Widok po fasetowaniu

and gemological properties were evaluated. Citrine is one of the natural quartz varieties containing iron (Weil 1984) (Figure 5). Pure quartz is colorless but can be found in various colors caused by some trace elements (Mn, Ti, Fe, and Cr) such as amethyst (purple-quartz), citrine (yellow-quartz), rose-quartz (pink-quartz), etc. (Monarumit et al. 2021; Kınacı and Ozturk 2023).

Like smoky quartz, natural citrines fade when heated above 200–500°C but turn yellow again when irradiated and gradually fade in UV light (Lehmann 1970). This indicates that the presence of color centers. At least some citrine is colored by aluminum-based and irradiation-induced color centers similar to those found in smoky quartz (Lehmann 1971; Maschmeyer et al. 1980). Since yellow color centers are generally more stable than smoky color centers, some smoky quartz can be converted to citrine by careful heating (Nassau and Prescott 1977).

The majority of citrine used in jewelry is produced artificially by heating amethyst to about 500°C. The precipitation of iron particles and interstitial Fe^{3+} defects in the quartz lattice increases when amethyst was heated (Cheng and Guo 2020; Shad 2021). Citrine's yellow hue can also be ascribed to the charge transfer band shifting into the visible band gap as a result of substitution centers changing into interstitial centers, in addition to these inclusions (Fe^{3+}) (Lehmann and Moore 1966). The color of citrines produced artificially in this way is more orange or reddish, unlike natural citrines, which are generally light/pale yellow (Ertik 2013).

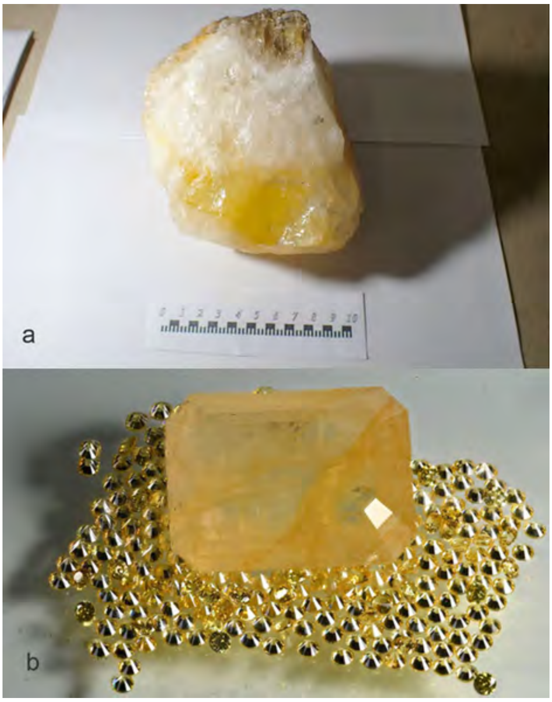

Fig. 5. a. Fe-Quartz transition before processing; b. Citrine after processing

Rys. 5. a. Przejście Fe-kwarc przed obróbką; b. Cytryn po obróbce

In some amethyst deposits, the amethyst has been partially or completely transformed into brown citrine by geothermal heating (Jenkins and Larsen 2004). Citrine can also be produced by heat-treating smoky quartz from certain regions (Chesterman 1979). It has also been suggested that iron is the cause of the color, as artificial crystals grown in an iron-containing solution turn orange (Rossman 1994). The amount of the two types of iron present in the quartz crystal depends on the growth direction and other growth factors (Nassau 1981). The color of both amethyst and citrine is due to the presence of iron in amounts of one part per million. Iron in the quartz structure replaces silica. Iron is trivalent and gives the yellow color seen in citrine (Jenkins and Larsen 2004). The color of citrine, a naturally rare type of quartz, is due to the iron content in its structure; hematite (Fe_2O_3) or limonite ($FeO(OH)nH_2O$) (Ertik 2013).

In the XRF analysis results performed on the sample, iron content was detected and the yellow color of the sample is due to the iron contained in it. Raman spectrometry results of Karacasu citrine evaluated in this study was found to be 175 cm^{-1}, 300 cm^{-1}, and 460 cm^{-1}. In Raman spectrometry studies the wavelengths in the Raman spectrometer were found to be 121 cm^{-1}, 200 cm^{-1}, and 462 cm^{-1} (Shad 2021). In addition, citrine was compared with Raman spectrometry in X080016 in the ruff database (Lafuente et al. 2015). When identifying geomaterials as gem-quality single crystals, FTIR is a very useful analytical method that is sometimes comparable to Raman spectroscopy. This is especially true for colored samples and the examination of surface treatments (Hainschwang 2016; Mercurio et al. 2017, 2018).

Generally speaking, diagnostic infrared bands are wider than those seen in Raman spectroscopy. These bands are typically found in the "finger-print region," which is a small spectral range (1,800–400 cm^{-1}). This spectral range makes it possible to identify gemstones visually, especially after gem cutting, by comparing the unknown spectrum to those in an appropriate spectral database (Izzo et al. 2020).

Although the Aydin region is small compared to the surface area of Turkiye, it hosts a large number of gemstones (quartz, smoky quartz, citrine, black tourmaline, almandine, etc.). Turkiye's largest quartz stones are found in this region.

Since the existence of gemstones is rare, they must be exceptional because of the environmental conditions that created them. Citrine, which has very distinctive yellow tones, is not widely available in the study area. Citrines, which do not have a wide distribution, could be observed in a narrow area on the outcrop surface, approximately 40–50 cm thick and approximately 1 meter long. According to the results obtained from the research conducted around it, it is rare to find.

It is considered that the citrine samples were broken off from a single large crystal because no crystal surfaces were detected on any part of the samples due to conchoidal fractures.

Citrine crystals developed within the metamorphics of the Menderes massif are remarkable with their impressive colors. However, it gains its real value through shaping after being extracted from nature.

Karacasu citrine crystals, which have similar optical and physical properties to other known citrine crystals, are important examples of semi-precious stones. Citrine is important for use because of its transparency, rarity, and brightness, and hardness.

Conclusions

Citrines can be found in the semi-precious/precious stone category, which can be easily distinguished from other ornamental stones with their yellow and shades of color and can gain a flashy appearance when processed. In this study, the geological and geochemical properties of these stones were evaluated together and investigated to be an important resource for future citrine studies and to reveal the potential of the reserve located in a narrow area in the Karacasu region of Western Anatolia (Turkiye). Although citrines are called ferrous quartz, they gain a striking appearance when they are faceted, polished, and turned into the final product in terms of ornamental stones.

The region, which is very rich in gemstones, can open an important economic area in terms of geotourism with the detection of citrine and similar new gemstone deposits.

Considering that most of the citrine used in the jewelry industry is obtained by heating amethyst, this deposit is very important in terms of natural citrine production.

It is thought that as a result of the geology and descriptions made in this study, similar places will be identified and will help find new deposits. It is considered that facing the collected samples in terms of lapidari means higher economic income.

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GEMOLOGICAL – GEOCHEMICAL CHARACTERISTICS OF WESTERN ANATOLIAN (KARACASU) CITRINES

Keywords

citrine, gemology, Karacasu, quartz, gemstone

Abstract

Gemstones have been valued by people for thousands of years, even before the science of geology was established. Ornamental stones are formed by elements commonly found in nature, such as oxygen, carbon, aluminum, silicon, and magnesium. Silica group gemstones, with the chemical formula SiO_2, are the most common gemstone group in the world. The presence of trace elements like Fe, Ni, Cr, and Cu gives them different colors. Quartz is a semi-precious inorganic gemstone that consists of Silicon dioxide (SiO_2) and crystallizes naturally, and it also stands out as a gemstone. In this study, the aim was to determine the geological, geochemical, and gemological properties of citrine formations in Western Anatolia (Karacasu–Aydin–Turkiye). In this context; XRF, Raman spectrum and FTIR studies were carried out to determine the chemical and gemological properties of the samples collected from the study area. According to studies; The iron content of citrines is between 0.05–0.07%. As a result of Raman spectrometry, wavelength results of 175 cm^{-1}, 300 cm^{-1}, and 460 cm^{-1} were obtained. In addition, it has been determined that citrine formations are in the form of thin veins in the crack zones at the contacts of the metamorphic units in the region. Yellow quartz crystals, which are gemologically identified as citrine, were shaped and their gemstone value was revealed. Although citrines are called ferrous quartz, they gain a striking appearance when they are faceted, polished, and turned into the final product in terms of ornamental stones. Given that, in the jewelry sector,

heat-treated stones, which are more affordable and readily accessible, are commonly used instead of citrine, it is believed that this study can provide significant insights into the characterization of the jewelry.

CHARAKTERYSTYKA GEMMOLOGICZNO-GEOCHEMICZNA CYTRYN Z ZACHODNIEJ ANATOLII (KARACASU)

Słowa kluczowe

cytryn, gemmologia, Karacasu, kwarc, kamień szlachetny

Streszczenie

Kamienie szlachetne są cenione przez ludzi od tysięcy lat, jeszcze zanim powstała nauka geologii. Kamienie ozdobne są tworzone przez pierwiastki powszechnie występujące w przyrodzie, takie jak: tlen, węgiel, aluminium, krzem i magnez. Kamienie szlachetne z grupy krzemionki, o wzorze chemicznym SiO_2, są najbardziej rozpowszechnioną grupą kamieni szlachetnych na świecie. Obecność pierwiastków śladowych, takich jak: Fe, Ni, Cr i Cu, nadaje im różne kolory. Kwarc jest półszlachetnym nieorganicznym kamieniem szlachetnym, który składa się z dwutlenku krzemu (SiO_2) i krystalizuje naturalnie, a także wyróżnia się jako kamień szlachetny. Celem tego badania było określenie właściwości geologicznych, geochemicznych i gemmologicznych formacji cytrynowych w zachodniej Anatolii (Karacasu–Aydin–Turcja).

W tym kontekście przeprowadzono badania XRF, widma Ramana i FTIR w celu określenia właściwości chemicznych i gemmologicznych próbek zebranych z badanego obszaru. Według badań, zawartość żelaza w cytrynach wynosi od 0,05 do 0,07%. W wyniku spektrometrii Ramana uzyskano wyniki długości fal 175 cm^{-1}, 300 cm^{-1} i 460 cm^{-1}. Ponadto ustalono, że formacje cytrynowe występują w postaci cienkich żył w strefach spękań na stykach jednostek metamorficznych w regionie. Żółte kryształy kwarcu, które z gemmologicznego punktu widzenia identyfikowane są jako cytryn, zostały ukształtowane i ujawniono ich wartość jako kamieni szlachetnych. Chociaż cytryny nazywane są kwarcem żelazistym, zyskują efektowny wygląd, gdy są fasetowane, polerowane i przekształcane w produkt końcowy w postaci kamieni ozdobnych. Biorąc pod uwagę, że w sektorze jubilerskim zamiast cytrynów powszechnie stosuje się kamienie poddane obróbce cieplnej, które są bardziej przystępne cenowo i łatwo dostępne, uważa się, że badanie to może dostarczyć istotnych informacji na temat charakterystyki biżuterii.