e-ISSN: 2687-6698

Research Article

Turkish Journal of Analytical Chemistry

TurkJAC

www.turkjac.org 2019

Usability of calcite mineral, which develops in the crack fillings of carbonate rocks, as ornamental stone

Murat Camuzcuoğlu

Bayburt University, Faculty of Applied Sciences, Department of Emergency Aid and Disaster Management, 69000, Bayburt, Türkiye

Abstract

Türkiye has a geologically significant amount of mineral content and offers essential resources, especially in the mining field (ornamental stone production). This study develops methods for extracting, processing, and usability calcite minerals, which develop as vein-filling (secondary formations) among fragmented limestones along the Bayburt-Erzurum highway for ornamental stone purposes. The chemical and crystallographic properties of the mineral were determined by XRD and FT-IR analyses. In the XRD analysis performed on the powder sample obtained from the mineral, a value of 80000 (cps) corresponding to 30 theta was found, which was determined to be a pure calcite mineral. In the FT-IR analysis performed to support the XRD analysis, peak values of 2513-1795 cm^{-1} and 1406-873-712 cm^{-1} were detected, and the value was observed to belong to the pure calcite mineral. Calcite mineral was used in jewelry production and was evaluated in terms of durability, aesthetics, and rarity in producing ornamental stones. Epoxy (durable, clean, and transparent) was used as a binding material in ornamental stone production. In general, calcite minerals are widely used in various industrial areas, but their use as ornamental stones is limited due to their low hardness. This study offers a new perspective on evaluating calcite minerals as ornamental stones, revealing that it is possible to process a low-hardness mineral as an ornamental stone using a binding material.

Keywords: Geology, calcite, ornamental stone, XRD analysis, FTIR analysis

1. Introduction

Ornamental stone refers to various colored rocks, minerals, and organic materials processed after being extracted from the earth's crust and used as ornaments and jewelry [1,2]. Ornamental stones are generally formed by abundant elements, such as carbon, aluminum, oxygen, silicon, magnesium, and calcium [2].

Hardness is essential when considering using minerals or stones as ornamental stones [3]. This is due to the necessity of processing, polishing, and preserving the stone's structure. For a material to be suitable for this purpose, it must be of a similar hardness to that of quartz, which has a Mohs hardness scale value of 7.

In particular, ornamental stones have been cut into various shapes, processed, and polished using multiple techniques, enhancing their visual appeal and appealing to people. They have also been used as a status marker throughout human history [4].

The study area is at the exit of Kop Mountain on the Bayburt-Erzurum Road and generally consists of thin, medium-layered, beige, yellowish, and brown-colored sandy limestones, thin-layered sandstones in green tones and gray-colored marl alternating clastic limestones. Limestones include the sandy levels in the north and south of the ultramafic massif and have a darker color than these units. Pure calcite mineral developed as veins in the crack fillings between clastic limestones.

The hardness of the calcite mineral is 3 according to the Mohs hardness scale, and its density is approximately 2.6 [5]. This mineral mainly forms the main mineral of carbonate rocks such as marble and limestone. Calcite mineral is mixed with different minerals (aragonite, etc.) with the same chemical content ($CaCO_3$), and such minerals with similar chemical content can be distinguished from each other by determining their chemical and crystallographic contents through XRD and FT-IR analyses. Today, calcite mineral is used in many sectors, such as paper, paint, construction, ceramics, food, and feed [5]. In addition to its uses in such sectors, it uses an ornamental stone. Pure crystalline calcite mineral generally occurs in the crack fillings of rocks existing in limestone formations, but it has yet to be produced commercially due to its small amount.

Citation: M. Camuzcuoğlu, Usability of calcite mineral, which develops in the crack fillings of carbonate rocks, as ornamental stone, Turk J Anal Chem, 6(1), 2024, 18–24.

https://doi.org/10.51435/turkjac.1489684

Author of correspondence: muratcamuzcuoglu@bayburt.edu.tr

Tel: +90 (458) 211 11 53

Fax: +90 (458) 333 20 43

Received: May 24, 2024

Accepted: June 11, 2024

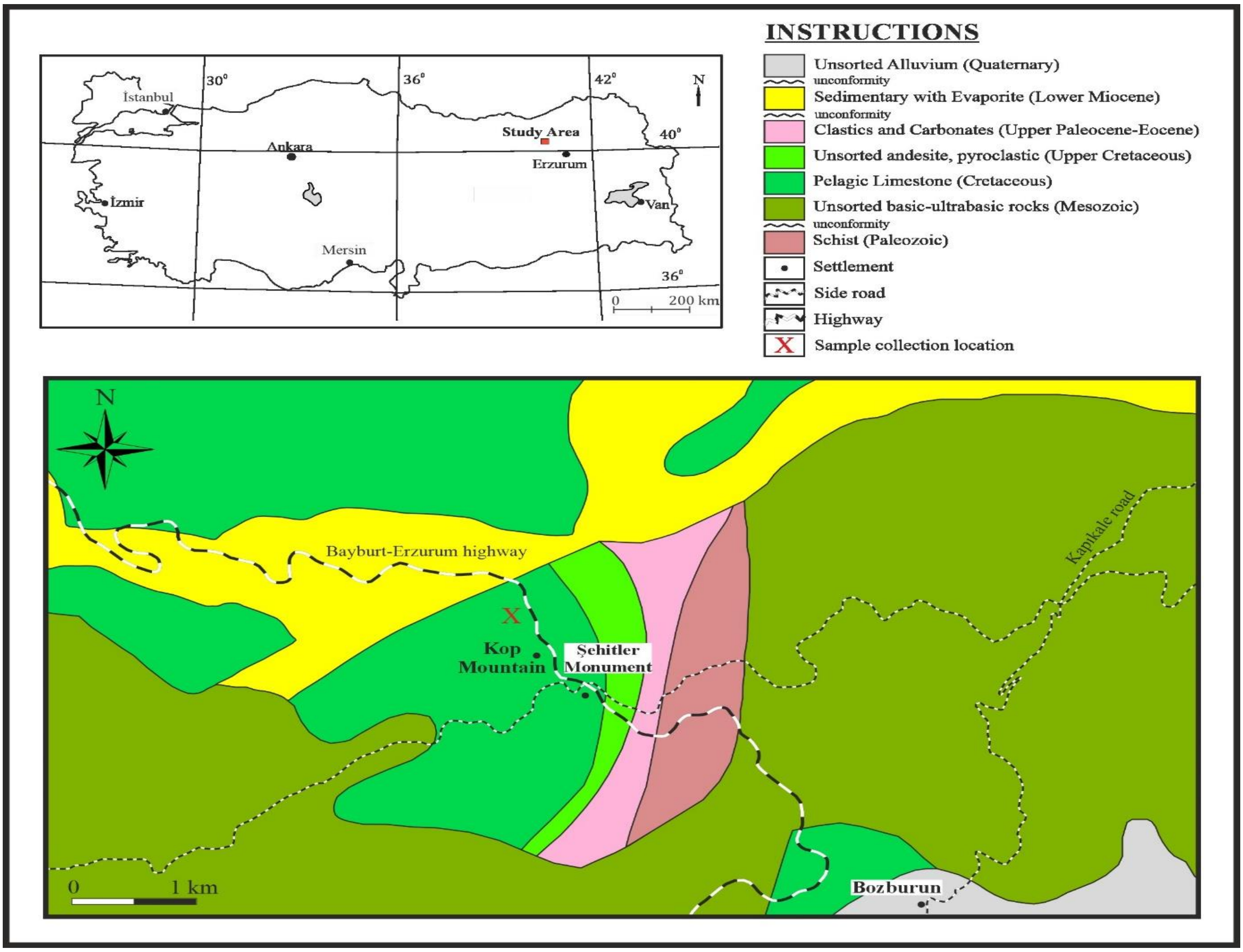

Figure 1. Modified study area location map

This study investigated the usability of pure crystalline calcite minerals occurring in crack fillings of limestone formation as ornamental stone (jewelry). The hardness of calcite is three, and the hardness of jewelry made by coating it with epoxy is determined to be 5.5-6. This hardness value is sufficient to harden the mineral that may be soft in jewelry production. Calcite minerals can be used as jewelry by being coated with epoxy when evaluated in terms of rarity and hardness. Studies in the literature generally examine composite materials, and in jewelry works, there are applications where powder paints are mixed with epoxy. This study has determined in the literature that new products can be obtained by bonding minerals with epoxy in jewelry making.

2. Material and methods

2.1. Material

It consists of pure crystalline calcite mineral, which develops as veins in the crack fillings between clastic limestones at the exit of Kop Mountain on the Bayburt-Erzurum Road and consists of $CaCO_3$ as its main element. The sampling location of the calcite mineral taken from the crack fillings of carbonate clastic rocks (Pelagic limestone) in the study area was recorded on the 1/25000 map taken from the Mineral Research and Exploration (MTA) earth sciences portal [6] (Fig. 1).

2.2. Preparation of calcite mineral for various applications

Since the pure calcite minerals taken in the study area developed in rock fillings, they were first removed (with the help of a hammer and tweezers) and made ready for analysis and gemstone applications. Since the calcite crystals will be used for ornamental stone application, they were carefully sorted to avoid damaging the crystal structure. During the sorting phase, the broken calcite crystals were pulverized in an agate mortar for XRD and FT-IR analyses, along with the ornamental stones produced from the powder sample.

2.3. Determination of XRD and FT-IR analyses

Calcite minerals from the field were ground in an agate mortar and turned into powder for XRD and FT-IR analyses. XRD and FT-IR analyses were conducted at Bayburt University Central Research Laboratory

Application and Research Center (BUMER). XRD Analysis was performed on a Bruker D8 Discover computer-controlled X-ray Diffractometer XRD to determine the mineralogical composition of the rock. For XRD analyses, diffraction Pattern Capture for Powder Samples took 1-30 minutes. The rock's chemical composition was determined using a PerkinElmer brand FT-IR spectrometer. In FT-IR analysis, vibrations occur between the bonds when infrared light interacts with matter. The energies from the vibrations are converted into spectra according to their wavelengths.

2.4. Production of ornamental stone

Epoxy resin was applied to the jewelry tool and allowed to dry slightly to make it easier to work. The crystals of the calcite mineral were arranged and prepared on a jewelry apparatus with the help of tweezers. No epoxy was applied to the calcite crystals on the surface to prevent them from losing their shine and naturalness. On the other hand, the calcite powder samples, which had been crushed and sieved, were poured into the prepared molds and filled. On the other hand, the epoxy resin prepared in a 2:1 ratio (epoxy and hardener) was poured into these molds. The epoxy was waited at 24 °C (at room temperature) for 24 hours and was allowed to dry, and after this period, the ready-made final products were removed from the molds.

2.5. Properties of the epoxy used

Epoxy resins are known for their high adhesion strength, chemicals, and water resistance. The epoxy used in the study is resistant to alkalis (concentrated and dilute), acids (dilute), solvent-containing substances (diesel, gasoline, alcohol, etc.), cleaning groups (disinfectant, detergent, etc.), oils (animal, vegetable, mineral) and seawater can show durability. For wet environments, epoxy can withstand temperatures up to 50 °C, while in dry environments, epoxy resin can withstand temperatures up to 130 °C. In the study, the application was made by mixing epoxy and hardener in a ratio of 2:1.

3. Geology

The study area covers Kop Mountain on the Bayburt-Erzurum highway. When the geology of the region is examined, there are unsorted basic-ultrabasic rock units belonging to the ophiolitic units represented by the Paleozoic-aged Schist rock unit at the base and the Mesozoic-aged units unconformably overlying it. These units are Cretaceous-aged Pelagic limestones overlie the sampling was done. The pelagic limestones from which the sampling was made were overlain by Upper Cretaceous-aged unsorted andesite and pyroclastic rock units and by Upper Paleocene - Eocene-aged clastic and carbonate units. Upper Paleocene-Eocene aged units were unconformably overlain by Lower Miocene aged evaporite sedimentary units, and all these rock units were unconformably covered by Quaternary-aged alluvial material. Since there was no detailed geological map or study in the study area, the map of the region was modified and drawn from the Earth Sciences Portal of Mineral Research and Exploration (MTA) [6] (Fig. 1). Sample collection in the study was carried out at the exit of Kop Mountain on the Bayburt - Erzurum Road towards Erzurum.

4. Results and Discussion

4.1. Ornamental stones

Ornamental stones (precious and semi-precious) have been popular for centuries due to their association with wealth and beauty. Some essential criteria are accepted worldwide for precious and semi-precious stones to be considered ornamental [7]. These criteria;

- The term ‘durability’ is defined as resistance to (external factors). This is represented by resistance to brittleness, impacts, and hardness.
- Beauty is inherently subjective, yet specific characteristics of the stone are universally regarded as aesthetically pleasing. These include its capacity for rapid processing, transparency, cleanliness, and a diverse array of attractive colors.
- Rarity is a critical factor in determining the value of a stone or an object.

In addition to the aforementioned essential criteria, several desired features are commonly sought in ornamental stones. These include the ability to reflect light (light refraction) and the ease with which they can be cut and polished. While no universally accepted definition differentiates precious stones from semi-precious stones, it is widely understood that stones such as sapphires, rubies, diamonds, and emeralds represent precious stones. Conversely, other stones are typically described as semiprecious stones. Sapphire, diamond, ruby, and emerald (precious stones) are considered noble when subjected to specific processes [8].

Ornamental stones result from various geological processes, including metamorphism, igneous activity, and hydrothermal activity. In magmatic and pegmatites, metamorphic rocks, and hydrothermal deposit areas, ornamental stones can be found on or near the surface [9]. Tectonic movements, such as faulting and volcanism, result in the stones being exposed at the Earth's surface.

While stones of natural origin are often the first thing that comes to mind when one thinks of ornamental stones, the term also encompasses materials of organic origin (pearl, amber, coral, etc.) and materials produced

Figure 2. Calcite minerals terrain view

synthetically (imitation) in a laboratory environment. Ornamental stones produced in laboratory environments have become a highly sought-after product worldwide in recent years. Natural stone is a material that is used extensively in the global market. It is frequently used to decorate interiors and exteriors, produce medical and dental products, and facade coatings. Moreover, natural stone's utilization in jewelry materials and ornaments is also rising. Consequently, further research is required to expand the use of natural (ornamental) stones, including semi-precious and precious stones.

Although a sub-discipline of mineralogy, Gemology is a branch of science that deals with ornamental stones and helps identify, examine, and classify materials. It is generally closely associated with stone cutting and jewelry making.

4.2. Macroscopic examinations

Coarse crystalline calcite minerals, which develop as veins in the crack fillings between the clastic limestones cropping out on the Bayburt-Erzurum Road, are observed in transparent white tones in the study area (Fig. 2).

Calcite minerals used as ornamental stones were carefully removed from the vein part of the rock to prevent their crystals from breaking. To ensure the homogeneity of the calcite crystals, small pieces were separated to prevent the crystals from being crushed too much. At the same time, any unwanted parts that could cause color were removed with tweezers. Then, the calcite minerals to be used as ornamental stones were set aside, and the remaining and very crushed calcite minerals were ground in an agate mortar for analysis and for producing ornamental stones from the powder sample (Fig. 3).

4.3. XRD analyses

X-rays are sent to the sample, which must have a smooth surface so that the X-rays are refracted and scattered at the right angle. The X-ray hitting the sample is reflected at different angles (α, β, γ) and intensities [10]. Thus, X-rays detect the mineralogical and elemental composition of the analyzed substance. From the peak values from quantitative calculations of the correct selection of different mineral parameters and the intensity ratio

Figure 3. Preparing the calcite mineral for ornamental stone production and chemical analysis

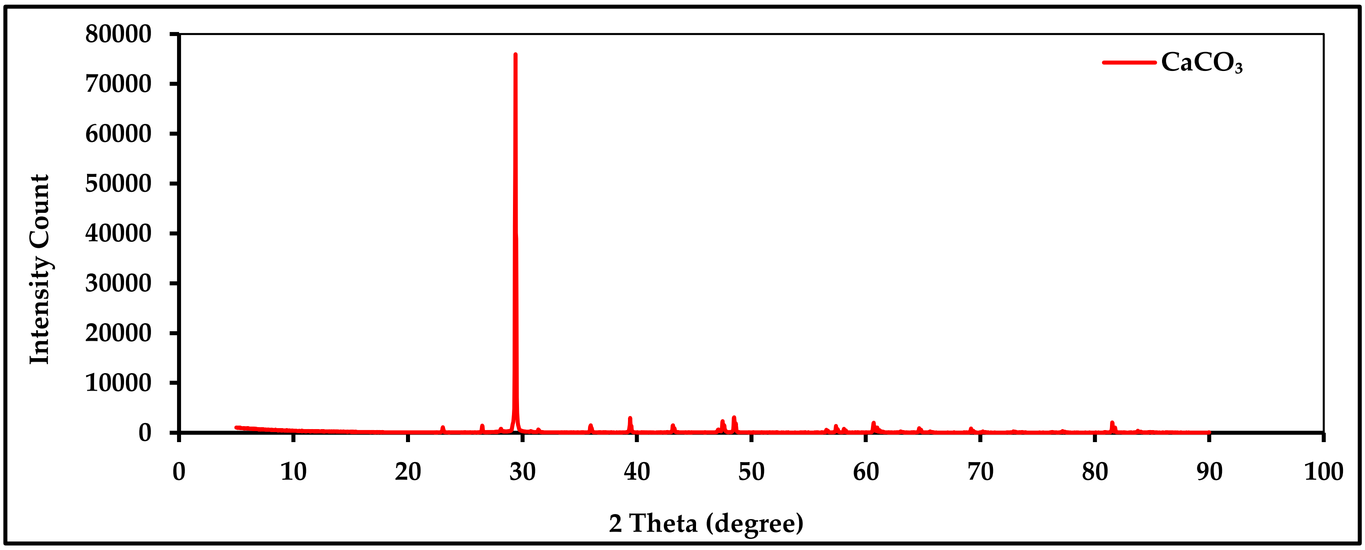

Figure 4. X-ray diffraction patterns of calcite

according to degree, the crystal system of the powder sample used and ground in the study was identified and determined to be a calcite mineral (Fig. 4).

Calcite and aragonite minerals are often confused due to their similar properties (structure and colors). Because these minerals are polymorphs of each other and have the same chemical composition ($CaCO_3$). The only distinguishing method is their crystal systems: calcite mineral crystallizes in the trigonal system, and aragonite mineral crystallizes in the hexagonal system. XRD analyses generally determine the elements and minerals in building materials, ores, and manufactured goods. As a result of XRD analyses, mineral names are determined using different crystal systems of minerals with the same chemical structure. In XRD imaging, the density of the coarse crystalline calcite mineral reaches up to 80000 (cps). The 80000 (cps) value reached is used to determine the purity of the calcite mineral and the calcite mineral. In the XRD analysis, the 80000 (cps) peak corresponds to the pure calcite peak compared to the 30-theta peak [11]. This high-density value increases depending on the prepared powder sample's surface orientation and the mineral's degree of crystallization. Although the same minerals are captured in some XRD images, the intensity varies depending on the purity of the mineral. The calcite mineral used in the study offers a density value close to pure.

4.4. FT-IR examinations

FT-IR spectroscopy allows for obtaining information about individual minerals and non-crystalline inclusions and detecting organic matter's presence. The absorption of IR by solids generally depends on the atom's strength, mass, and length of the interatomic bonds in the structure of the minerals. Additionally, it is subject to the constraints of the global symmetry of the local and the unit cell site symmetry (site symmetry) of each other atom within the unit cell [12]. Furthermore, the absorption of IR is significantly influenced by the size and shape of the mineral particles [13] and, to a certain extent, by the crystalline arrangement [14]. In the FT-IR analysis, the sample examined was not a rock but a mineral, so no peak value of any foreign material was obtained. In FT-IR spectroscopy, which can provide some helpful information about the structure of the molecules, it appears to have absorption bands at 2513-1795 cm^{-1}. Moreover, Asymmetric peak values of 1406-873-712 cm^{-1} were reached. IR spectra are consistent with the characteristic vibrations of calcite [15,16]. The peak values by the FT-IR analysis showed that the examined sample had pure $CaCO_3$ content and supported the XRD measurements (Fig. 5).

4.5. Gemstone applications

The study proposed that by binding natural stones or minerals with different binding materials, their usability as ornamental stones would be enhanced in terms of visual appeal by imparting various properties such as shine and durability. For this purpose, epoxy has been selected due to its high resistance to multiple chemicals and temperatures and ease of workability and cleanability (transparency). In addition to its strength and durability, which have been widely utilized recently, epoxy exhibits these properties. Epoxy is employed in a multitude of applications, including exterior coatings, the production of adhesives for forest products (furniture, wood, etc.), high-performance floors (waterproof floors, mosaic floors, colored aggregate flooring, chip flooring etc.), the construction industry (paint, lining, coating, etc.), aviation, industry, and the space industry. Furthermore, epoxy is employed in numerous artistic and decorative areas. In the creative field, various products, including earrings, coasters, necklaces, and rings are produced by combining different colors into epoxy resins. Nevertheless, further

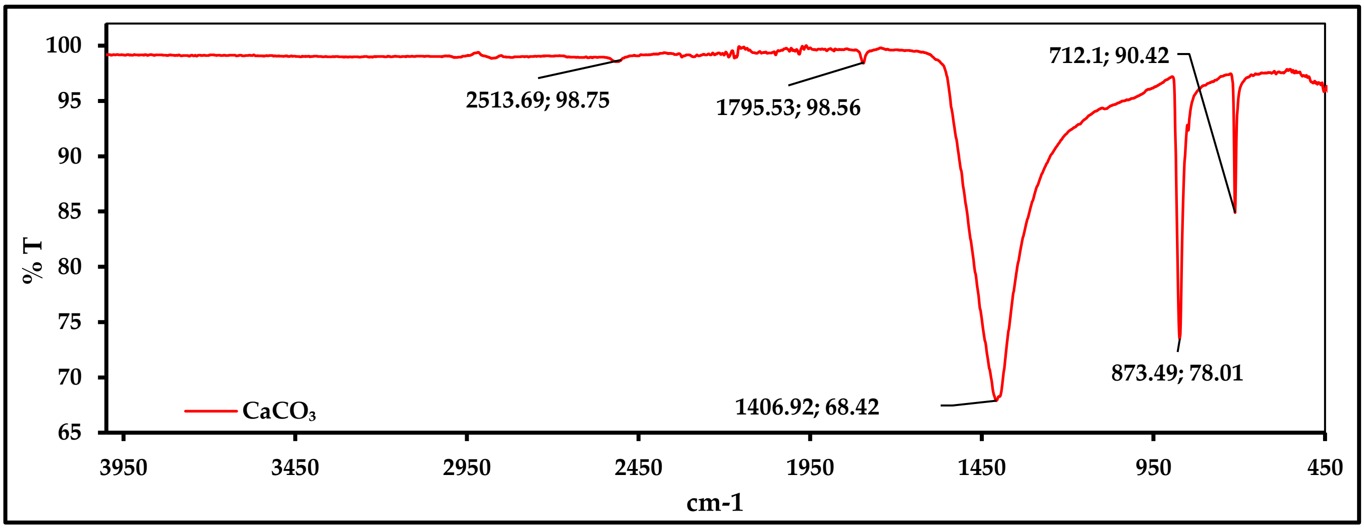

Figure 5. Fourier transform infrared spectroscopy (FT-IR) spectra: $CaCO_3$ (Calcite)

studies are required to expand the knowledge base on jewelry products with epoxy binders made using natural minerals. In this study, the excellent adhesion properties and durability of the epoxy used as a binder were employed to enhance the durability of the low-strength calcite mineral. Furthermore, minerals with low hardness can be utilized as ornamental stones by imparting them with distinctive properties due to epoxy binder material.

The color content of the coarse crystalline calcite observed in the study area, its pure, clean, bright, and transparent appearance, its ability to be quickly processed, and its less (in secondary rock vein fillings) make it rare. These properties of the calcite mineral increase its usability as an ornamental and jewelry material and show that it has an economic value. Although there is a cost of using epoxy in jewelry production, the cost of epoxy can be neglected because the product obtained using calcite mineral is valuable.

The study obtained two products (calcite crystal and powder) using calcite as an ornamental stone (Fig. 6a). In accessory products made from calcite powder samples (ring stone, pendant, etc.), calcite powder reacted with epoxy and caused a color change (white-yellow) (Fig. 6b). No color change was observed in the accessory product made of calcite crystals (Fig. 6c). Ornamental stone production involves combining natural minerals with various binding materials, and more research and development are needed for these processes.

5. Conclusions

A classification of the usability of the product obtained from the study as jewelry (bracelet, earring, and ring stone) according to the existing categories in the classification of ornamental stones is presented below.

- In terms of durability, the hardness of calcite is 3. Although it has low strength, it has been found that calcite is suitable for use in jewelry making as the epoxy used as a binding material has sufficient chemical and physical resistance.
- Although visuality is a relative concept, the calcite mineral's crystalline structure increases the product's visuality and potential as a gemstone.
- In terms of rarity, although calcite mineral is not rare compared to other precious and semi-precious minerals, it can be considered valuable due to its secondary formation and formation in crack fillings of detrital limestones (occurrence in small amounts).

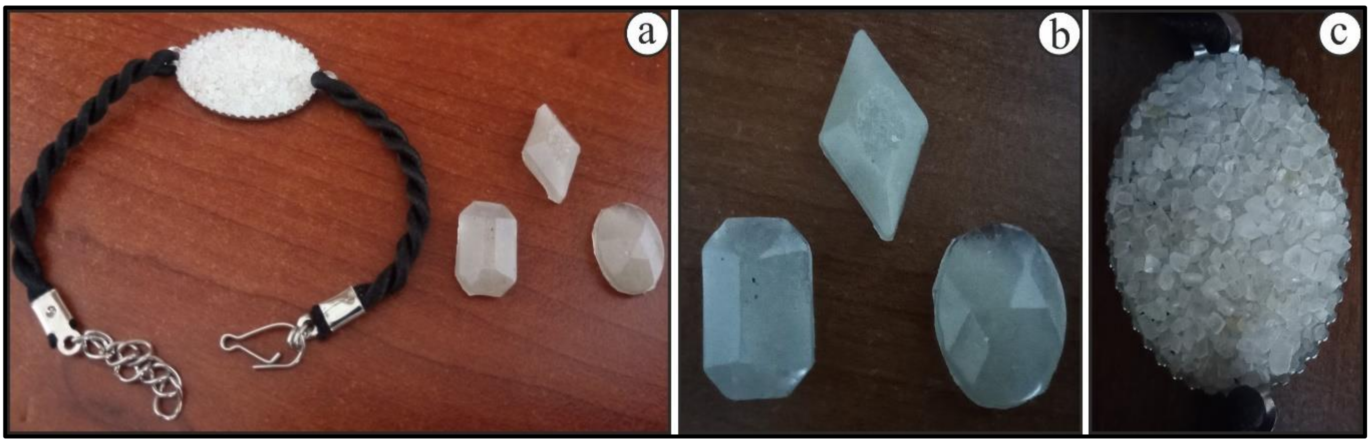

Figure 6. a) Jewelry produced in calcite mineral, b and c) Close-up photographs of the jewelry made

As a result, this study shows that the low-hardness calcite mineral (coarse crystalline and developing secondary in rock crack fillings) with different usage areas can be used as a gemstone by bonding with a binding material (epoxy). Furthermore, it has been established that the epoxy employed as a binder can be utilized for diverse applications in the fabrication of ornamental stones, encompassing both cleanliness (transparency) and durability (chemical and physical resistance).

References

[1] Y. Eşme, Anadolu'da Bilinen Önemli Süstaşları Jeolojik ve Ekonomik Potansiyeli (Unpublished), Bornova, İzmir, 1994.

[2] İ.K. Akbudak, Z. Başıbüyük, M. Gürbüz, Yozgat "Aydıncık" kalsedon-ametist oluşumlarının mineralojisi-petrografisi ve ekonomikliliğinin incelenmesi, DÜMF Mühendislik Dergisi 9(1), 2018, 313-324.

[3] S. Ghorbani, S.H. Hoseinie, E. Ghasemi, T. Sherizadeh, A review on rock hardness testing methods and their applications in rock engineering, Arab J Geosci, 15 (11) (2022).

[4] M. Camuzcuoğlu, Peridotitin Epoksi (Reçine) İçerisinde Renk Verici Pigment Olarak Kullanılabilirliği ve Süstaşı Yapımı, European Confereces 2nd International Conference on Health, Engineering and Applied Science, 4-6 August, Belgrade, 2023.

[5] Mineral Research and Exploration (MTA), Türkiye, 2024, https://www.mta.gov.tr/v3.0/bilgi-merkezi/kalsit (Access; 18.05.2024)

[6] Mineral Research and Exploration (MTA), Yerbilimleri, Türkiye, 2024 http://yerbilimleri.mta.gov.tr/anasayfa.aspx (Access; 27.04.2024)

[7] T. Rızaoğlu, M. Camuzcuoğlu, Usability of Obsidian with Special Refraction as an Ornamental Stone by Bonding with Epoxy Resin, Systemy Wspomagania w Inżynierii Produkcji, 11(2), 2022, 96-103.

[8] https://www.mta.gov.tr/v3.0/bilgi-merkezi/sustasi (Access; 12.05.2024)

[9] C. Simonet, E. Fritsch, B. Lasnier, 2008). A classification of gem corundum deposits aimed towards gem exploration, Ore Geol Rev, 34 (1-2), 2008, 127-133.

[10] W. Harris, W.G. Norman, X-ray diffraction techniques for soil mineral identification. In Methods of Soil Analysis Part 5-Mineralogical Methods, American Society of Agronomy and Soil Science Society of America, 2015, 81-115.

[11] MinDAT 2024 https://www.mindat.org/min-859.html (Access; 07.06.2024)

[12] D.S. Volkov, O.B. Rogova, M.A. Proskurnin, Organic Matter and Mineral Composition of Silicate Soils: FTIR Comparison Study by Photoacoustic, Diffuse Reflectance, and Attenuated Total Reflection Modalities, Agronomy, 11(9), 2021,1-30.

[13] M. Fan, D. Dai, B. Huang, Fourier transform infrared spectroscopy for natural fibres. Fourier transform-materials analysis, 3, 2012, 45-68.

[14] R. Bardestani, G.S. Patience, S. Kaliaguine, Experimental methods in chemical engineering: specific surface area and pore size distribution measurements-BET, BJH, and DFT, Can J Chem Eng, 97(11), 2019, 2781-2791.

[15] D. Shan, S. Wang, H. Xue, S. Cosnier, Direct electrochemistry and electrocatalysis of hemoglobin entrapped in composite matrix based on chitosan and $CaCO_3$ nanoparticles. Electrochem Commun, 9, (2007), 529-534.

[16] S. Hajji, T. Turki, A. Boubakri, M. Ben Amor, N. Mzoughi, Study of cadmium adsorption onto calcite using full factorial experiment design, Desalin Water Treat, 83, (2017), 222-233.