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Surprise eggs, the miracle of nature: almus agates (Tokat – Turkiye)

Introduction

Silica group gemstones are the most common gemstone group in the world. The chemical formula of silica group gemstones is SiO_2. The most important factor for the members of this group to be of different colors is that they are accompanied by trace amounts of different elements (Fe, Ni, Cr, Cu etc.), which are the trace elements in their chemical content (Götze et al. 2001, 2004; Caucia et al. 2016; Başıbüyük 2018; Kaydu Akbudak et al. 2018). Another factor that makes a difference is diversification resulting from the formation of these members in crystalline, cryptocrystalline or amorphous forms (Graetsch 1994; Hatipoğlu et al. 2010). For this reason, silica group ornamental stones can create

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a large number of products with different colors and textures according to their trace element content and formation forms. Agates, which are a member of this group, are usually found in volcanic rocks and they either form during hydrothermal processes (Hatipoğlu et al. 2011; Götze et al. 2012) or in sedimentary/diagenetic environments (Moxon 2002; Moxon and Reed 2006; Çalık and Arzoğulları 2014). Sometimes, they can be found in metamorphic rocks (Moxon et al. 2006). Agates can grow in very vivid colors and a wide variety of colors and textures and can contain color zones in concentric banding. Treatment methods are used in pale-colored agates that are not considered to be visually sufficient. Therefore, color treatments are made in agates by methods such as dyeing and heat treatment (Hajalilou and Vosug 2008; Yazdi, et. al. 2016).

The Tokat region where the Almus agates are located is a very rich field in terms of silica-containing gemstones – blue-banded-druse-geod structured chalcedonies, nodular-banded-moss agates, chrome chalcedony (Başıbüyük et al. 2020), silicified woods (Kaydu Akbudak et al. 2017), jaspers of various colors (Yüzbaşıoğlu 2020). Almus agates have a different place in the agate world with their unique colors and textures. This study aims to share the formation and gemological characteristics of Almus agates found in Eocene-aged volcanic rocks in the north of Anatolia in the form of nodules of different shapes and sizes with the scientific world and agate lovers.

1. Method and materials

Field studies were carried out in the northern and northeastern regions of the Tokat province and agate samples were collected. Thin sections were made in Kırşehir Ahi Evran University Geological Engineering and thin-section laboratory and petrographic examinations were carried out. Field emission scanning electron microscope (FE-SEM) analysis was performed on four agates (K-6, 10, 14, 21) and one host rock (K-2) samples selected from the samples taken from the study area. Image, point and multipoint eds values were obtained from the samples and XRF (X-ray fluorescence) analyses have been made at Mersin University MEİTAM (Mersin University Advanced Technology Education, Research and Application Center) to provide geochemical and mineralogical characterizations of the gemstones.

2. Geology

In the Almus (Tokat-Turkiye) area, basement units consist of the Paleozoic-Mesozoic Tokat Massif and Bakımlıdağ Complex units (Yılmaz 1984; Bozkurt and Koçyiğit 1996; Özcan and Aksay 1996; Yılmaz et al. 1997; Sümengen 2013a, b; Göçmengil et al. 2018). The Tokat Massif is comprised of low-grade metamorphic units which are represented by metabasite, marble, serpentinite, mica-schist, amphibolite and scarce blueschist. The Bakımlıdağ

Complex is made up of gabbro, serpentinite and cross-cutting dolerite dikes (Göçmengil et al. 2018). All these basement units are unconformably overlain by middle Eocene volcano-sedimentary successions (Bozkurt and Koçyiğit 1996; Göçmengil et al. 2018). Neogene sedimentary units and Quaternary sedimentary successions are the youngest units in the area and unconformably overlain by the older units (Göçmengil et al. 2018). Almus agates are found in Eocene Trachytes belonging to Almus volcanics (Figure 1).

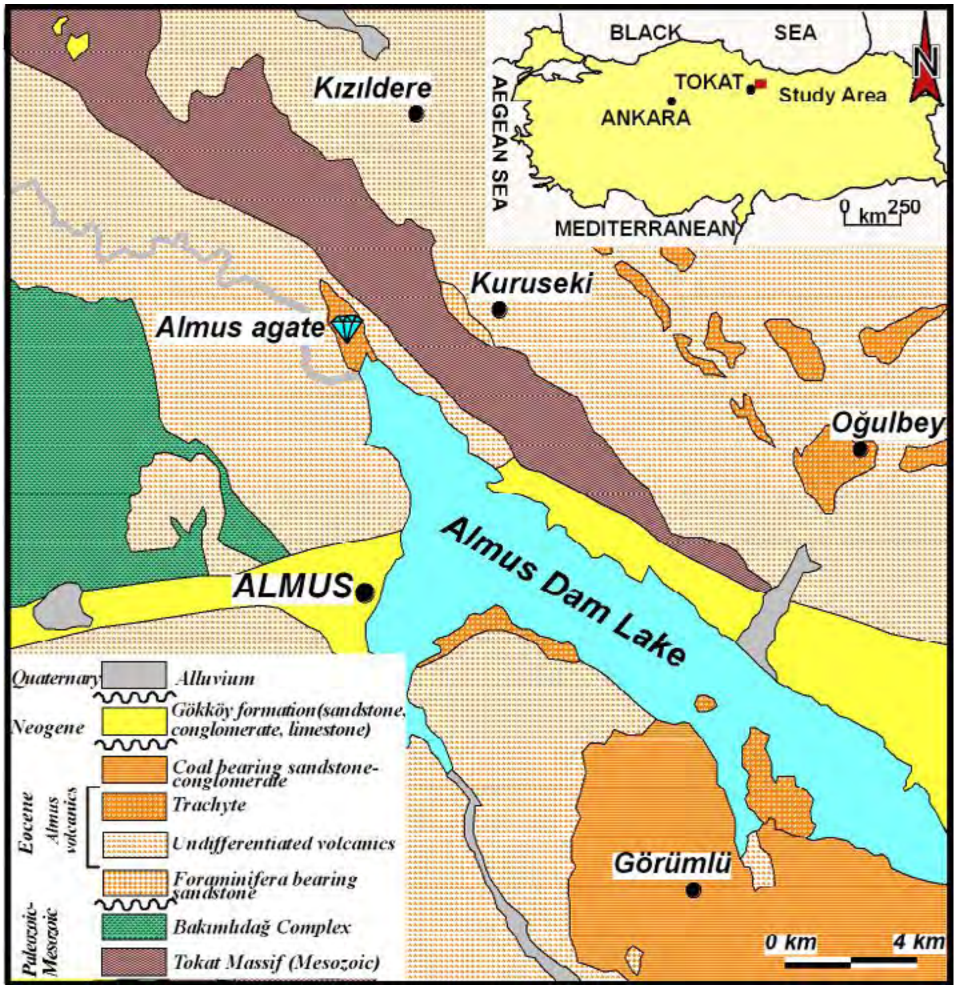

Fig. 1. Geological map of the study area
(Bozkurt and Koçyiğit 1996; Sümengen et al. 2013a, b; Göçmengil et al. 2018)

Rys. 1. Mapa geologiczna badanego obszaru

3. Results

3.1. Field studies

Almus agates were formed as nodules in the form of drop-spheres in the pores within the light brown-gray colored trachytes (Figure 2a–d) of Eocene age (Figure 2e–h). The outer

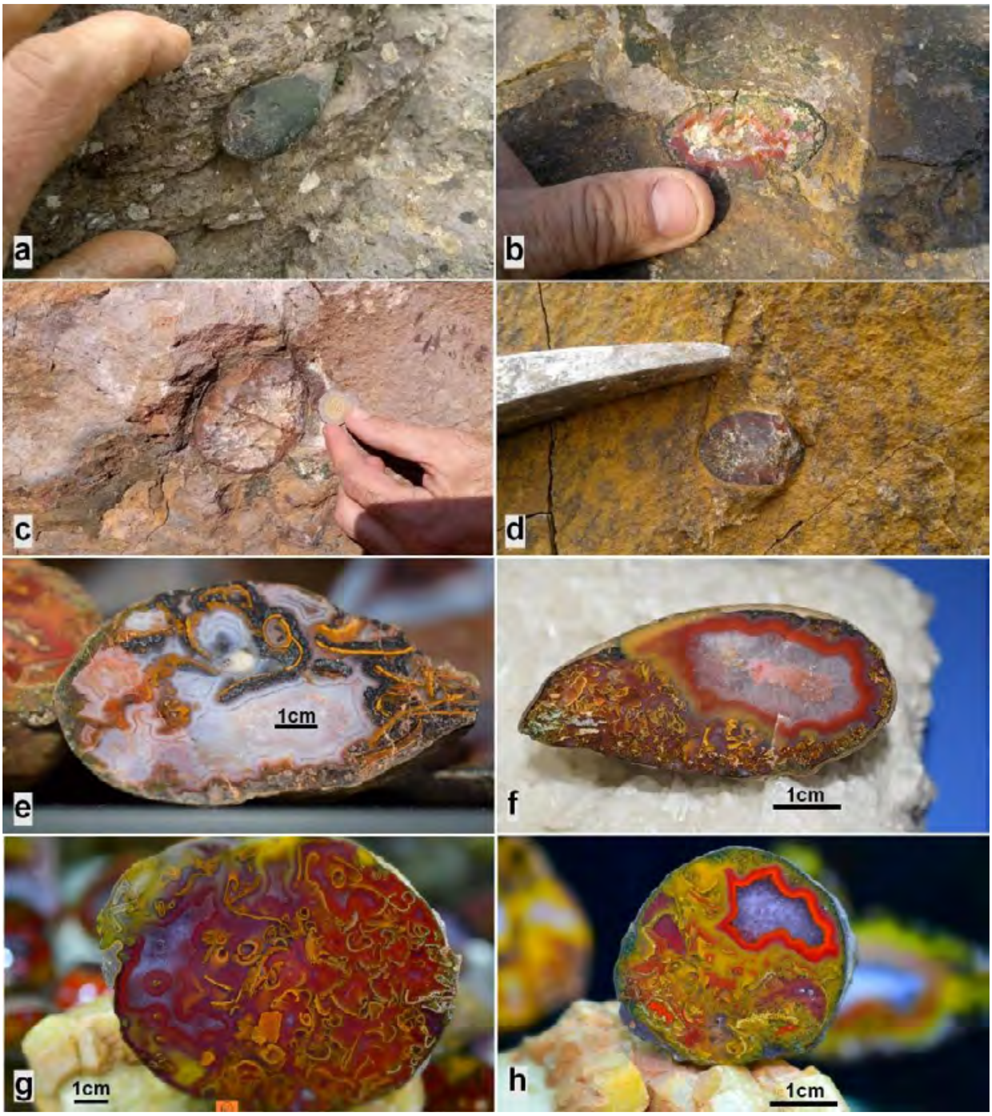

Fig. 2. Almus agates formed in drop-spherical form in volcanic host rocks (Trachyt)

Rys. 2. Agaty Almus uformowane w postaci kulistej kropli w wulkanicznych skałach macierzystych (trachyt) parts of the Almus agates are of such colors as green, brown, yellow and red, while their interior parts can be in many different colors and tones such as gray, white, blue, lilac, red, yellow and orange. These formations are observed in sizes ranging from a few centimeters to 25–30 centimeters. Macrocrystalline quartz is also found in the central parts of some Almus agates. It was observed in fine-grained pyrite minerals in some agate nodules.

3.2. Mineralogy

According to petrographic studies, the host rock (trachyt) shows microlitic porphyritic, locally glomeroporphyric texture and flow texture (trachytic texture). Alkali feldspar (sanidine), plagioclase microlites and small opaque minerals (pyrite) were distinguished in the sections (Figure 3). It is composed of alkali feldspars and there are no mafic minerals as phenocrysts. The groundmass consists of volcanic glass, opaque minerals and feldspar microcrystals. The pores are filled with calcite, iron oxide and quartz in places.

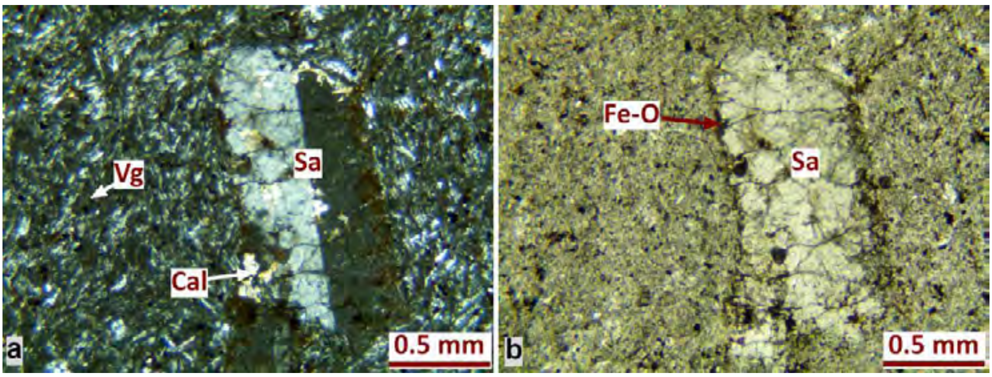

Fig. 3. Sanidine phenocrysts in volcanic host rocks

Rys. 3. Fenokryształy sanidyny w wulkanicznych skałach macierzystych

Calcite and iron oxide fill in drop (Figure 4 a) and sphere (Figure 4 b) pores. There are iron oxide minerals in the broken zones within the calcite filling formed in the pores (Figure 4).

It was observed that silica minerals replaced calcite minerals in some pores filled with ironoxide-calcite in volcanic host rocks (Figure 5a–d). This situation helps us to explain how the fossil-like formations observed in Almus agates came into being. In the thin-section studies performed on samples containing fossil like structures, it was observed that these structures consist of opaque minerals (iron oxide minerals). In Figures 5c and d, calcite minerals are replaced by silica minerals. It is observed that iron-oxide minerals remain in their places.

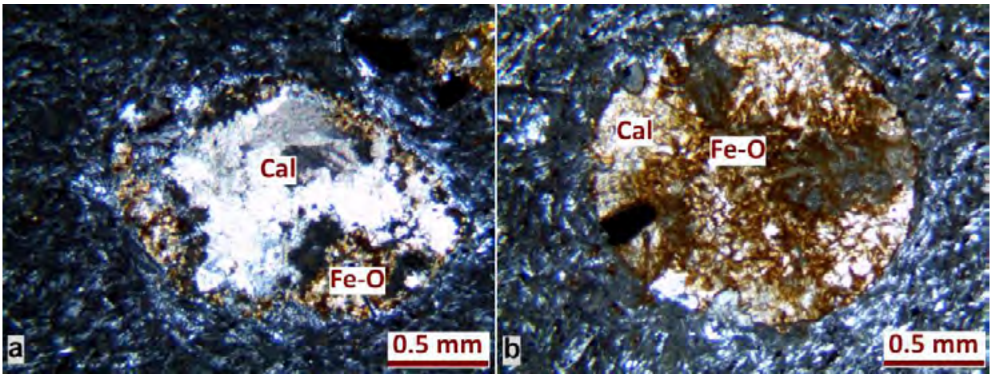

Fig. 4. Iron oxide and calcite filling formed in pores in volcanic host rocks

Rys. 4. Wypełnienia z tlenku żelaza i kalcytu utworzone w porach w wulkanicznych skałach macierzystych

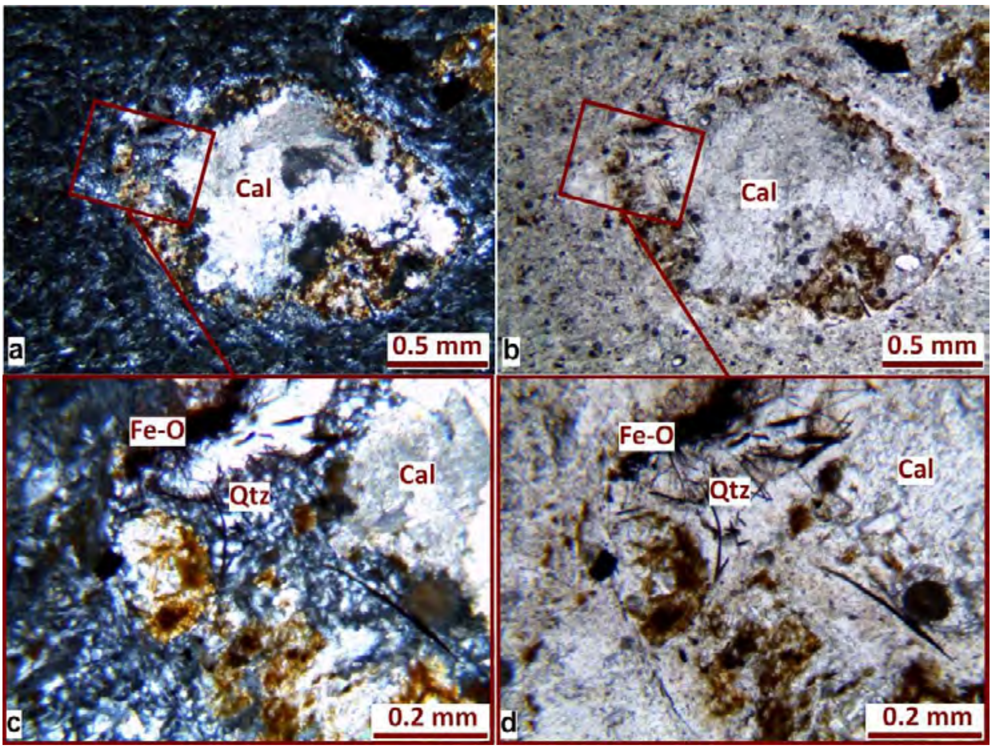

Fig. 5. Silica minerals replacing calcite minerals in iron-oxide-calcite filled pores in volcanic host rocks

Rys. 5. Minerały krzemionki zastępujące minerały kalcytu w porach wypełnionych tlenkiem żelaza i kalcytem w wulkanicznych skałach macierzystych

During agate formation, cryptocrystalline-microcrystalline quartz bands with tones of different colors are generally formed on the outer walls of the pore, and coarse crystalline quartz is formed in the inner parts (Figure 6).

Almus agates are mainly composed of cryptocrystalline-fibrous quartz (Figure 8a, b) as length-slow zebraic chalcedony and quartzine (Powolny et al. 2019; Pršek et al. 2020). In this study, we present a formation model of Almus agates. Firstly, iron-oxide veins (skeletal structure) formed with calcite minerals in the pores (Figures 4 and 5). This skeleton structure behaved like a host rock during agate formation, and quartz in contact with iron-oxide formations were formed in a crypto-microcrystalline structure like those formed in the

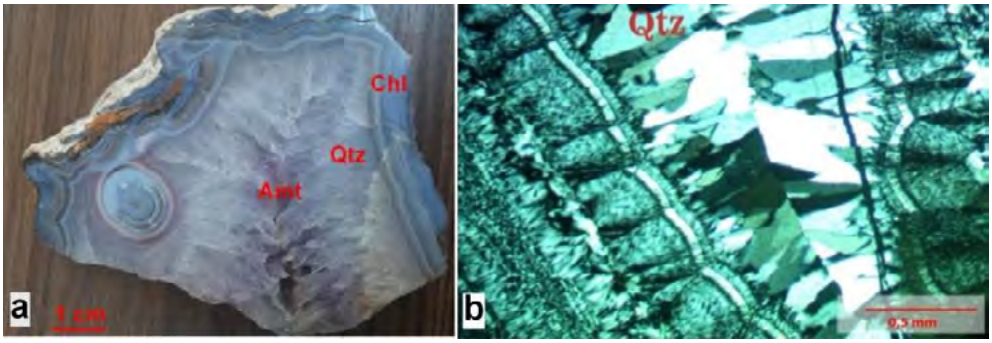

Fig. 6. Aydıncık agate with cryptocrystalline-microcrystalline outer part and macro crystalline quartz inside
a – macro view, b – thin section view (Akbudak et al. 2018; Başıbüyük 2018)

Rys. 6. Agat Aydıncık z kryptokrystaliczno-mikrokrystaliczną częścią zewnętrzną i makrokrystalicznym kwarcem wewnątrz
a – widok makro, b – widok cienkiego przekroju

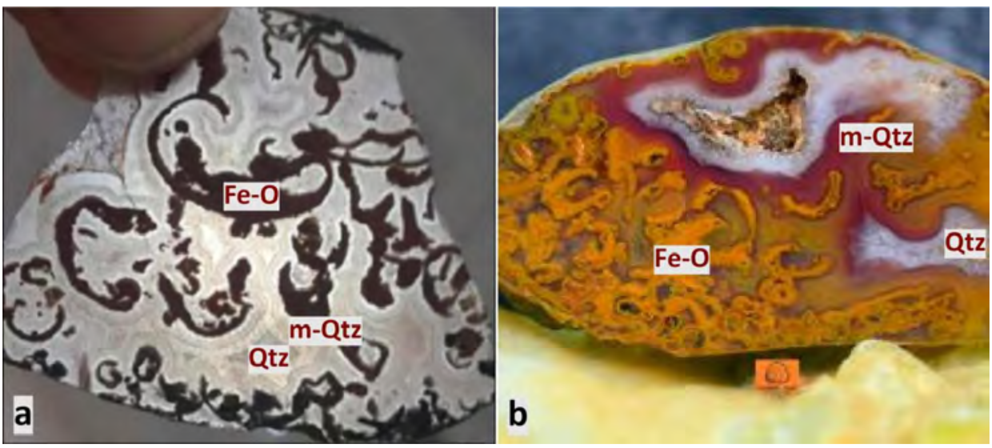

Fig. 7. Almus agates containing fossil like structures
Fe-O – iron oxide formations, Qtz – quartz, m-Qtz – microcrystalline quartz

Rys. 7. Agaty Almus zawierające struktury podobne do kopalnych
Fe-O – formacje tlenku żelaza, Qtz – kwarc, m-Qtz – kwarc mikrokrystaliczny

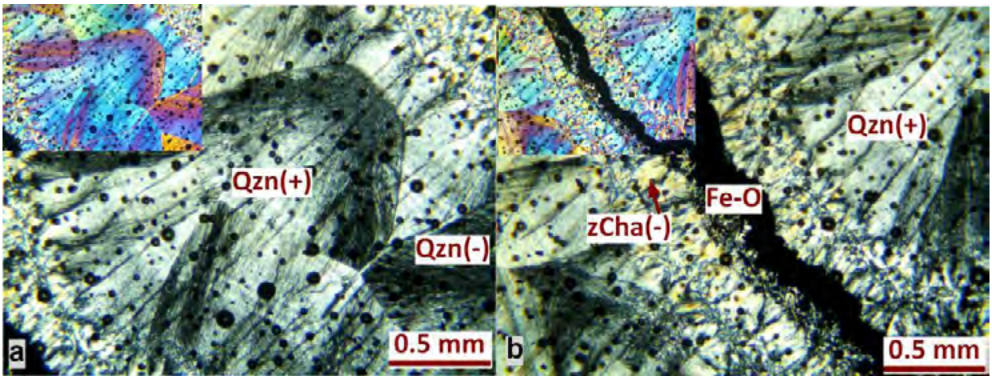

Fig. 8. Thin section images of agates containing fossil like structures
Fe-O – iron oxide formations, Qzn – quartzine, zCha – zebraic chalcedony

Rys. 8. Cienkie przekroje agatów zawierających struktury podobne do kopalnych
Fe-O – formacje tlenku żelaza, Qzn – kwarcyt, zCha – zebrowy chalcedon

walls of the host rock (Figures 7 and 8b). Fossil-like structures were formed in the pores where iron-oxide veins were thick (Figure 8b). It is surrounded by a microcrystalline quartz zone at the contacts of the iron-oxide formations (Figure 8b). In some areas, the iron-oxide skeleton has reacted with the incoming siliceous solution and as a result, a sieve-like texture was formed (Figure 8b). The siliceous solution in the fine-grained pores where iron-oxide formations are concentrated replaced the calcite minerals and caused the formation of different colored zones consisting of microcrystalline quartz.

3.3. SEM and Geochemistry

As a result of the FE-SEM analysis performed on the K-6 sample consisting of brown--yellow-red colors (Figure 9), it was observed that the quartz in the brown region had coarse crystals and the quartz in the yellow and red regions were fine crystalline. As a result of the EDS analysis, it was determined that the quartz was composed of Si and O with a trace of Fe. The proportions of trace elements that may have caused the color change could not be determined by this method. A similar situation was observed in the results of FE-SEM analyses performed in samples K-10, K-14 and K-21 (Figure 10). The highest iron content was measured in the yellow field at sample K-14. When the image and geochemical results are evaluated together in the measurements made from the host rock (sample K-2), ilmenite in Figure 11 (on the left) and clay mineral in Figure 11 (on the right) are shown.

According to the results of XRF analysis, host rock (trachyte) has a geochemical composition of SiO_2 (59.38 wt.%), Al_2O_3 (18.11 wt.%), K_2O (7.68 wt.%), Fe_2O_3 (5.60 wt.%), Na_2O (4.61 wt.%) and CaO (2.61 wt.%). Fine crystalline parts of Almus agates are mainly composed of SiO_2 (98.22 wt.%), Fe_2O_3 (1.42 wt.%), Cr_2O_3 (0.17 wt.%), Al_2O_3 (0.095 wt.%)

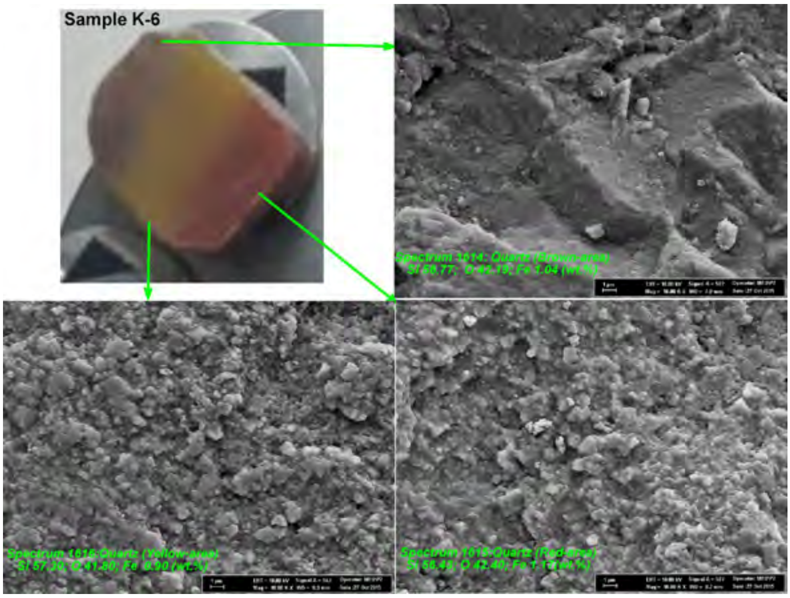

Fig. 9. Image and multipoint EDS values of the sample containing brown, yellow and red tint bands, Sample K-6

Rys. 9. Obraz i wielopunktowe wartości EDS próbki zawierającej brązowe, żółte i czerwone pasma zabarwienia, próbka K-6

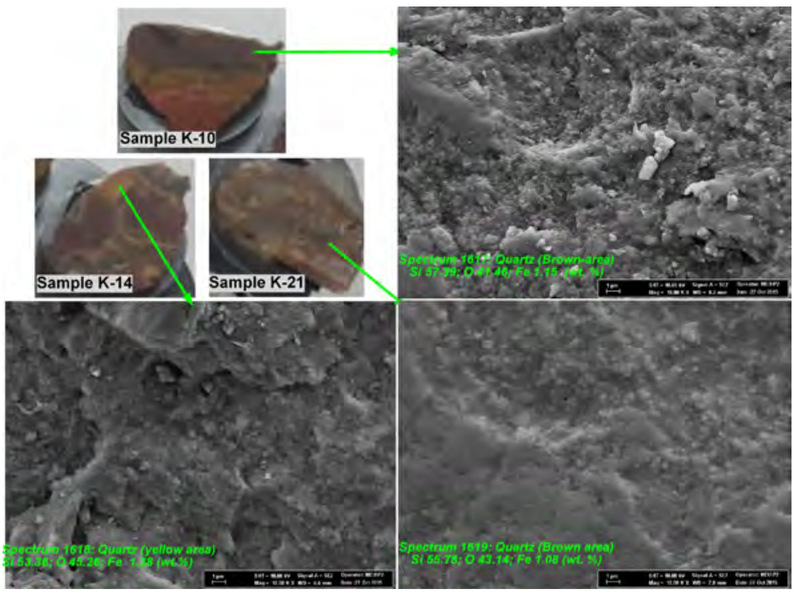

Fig. 10. Image and multipoint eds values of samples containing brown and yellow tint bands, Sample K-10, K-14, K-21

Rys. 10. Obraz i wielopunktowe wartości EDS próbek zawierających brązowe i żółte pasma, próbka K-10, K-14, K-21

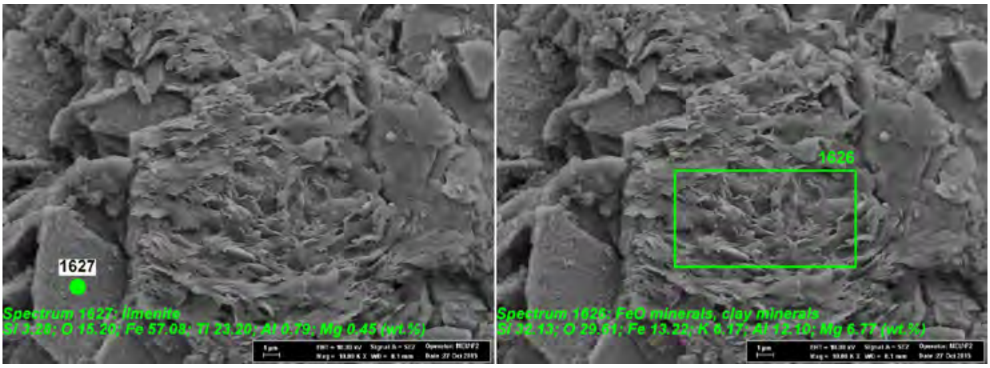

Fig. 11. Image and point-multipoint EDS values in the host rock sample, Sample K-2

Rys. 11. Obraz i wartości punktowo-wielopunktowe EDS w próbce skały macierzystej, próbka K-2

and CaO (0.039 wt.%) while coarse crystalline parts have geochemical composition SiO_2 (98.69 wt.%), Fe_2O_3 (0.96 wt.%), Cr_2O_3(0.13 wt.%), Al_2O_3 (0.15 wt.%) and CaO (0.049 wt.%).

3.4. Gemology

Almus agates, which contain quite different and vibrant colors, are massive and have a waxy luster. While some of the samples have a microcrystalline structure, there are still others which have a micro- and macro- crystalline structure together. When evaluated in terms of color zoning, textural properties, hardness, durability and machinability, it was determined that Almus agates can be used as a gemstone in jewelry and accessories production.

Some of the Almus agates taken from the study area were processed in the Ümit Ulus gemstone shaping workshop; jewelry and accessory objects were produced (Figure 12, 13).

Conclusions

Almus agates are found in Eocene Trachytes belonging to Almus volcanics. Trachytes have hypocrystalline hypidiamorphic porphyritic texture (trachytic texture). There are no mafic minerals as phenocrysts; alkali feldspar (sanidine), plagioclase microlites, small opaque minerals are present in trachytes. The pores are filled with calcite, iron oxide and quartz in places.

Almus agates consist of cryptocrystalline-fibrous quartz as length-slow zebraic chalcedony and quartzine. The presence of length-slow chalcedony and pyrite suggest that the fluids forming the agates are alkaline and/or Mg/SO_4-rich solutions (Powolny et al. 2019).

Table 1. XRF analysis results (wt.%) of Trachyte (host rock) and Almus agates in the study area

Tabela 1. Wyniki analizy XRF (% wag.) trachitu (skały macierzystej) i agatów Almus na badanym obszarze

		K4 (host rock) 	K15 (fine cryst. outer zone) 	K15 (coarse cryst. interior) 
Na_2O	(wt.%)	4.61	0	0
MgO	(wt.%)	0.50	0	0
Al_2O_3	(wt.%)	18.11	0.095	0.15
SiO_2	(wt.%)	59.38	98.22	98.69
P_2O_5	(wt.%)	0.35	0	0
SO_3	(wt.%)	0.032	0.021	0
Cl	(wt.%)	0.079	0	0
K_2O	(wt.%)	7.68	0.014	0.022
CaO	(wt.%)	2.61	0.039	0.049
TiO_2	(wt.%)	0.83	0	0
MnO	(wt.%)	0.093	0	0
Cr_2O_3	(wt.%)	0	0.17	0.13
Fe_2O_3	(wt.%)	5.60	1.42	0.96
CuO	(wt.%)	0.009	0	0
ZnO	(wt.%)	0.014	0.010	0.004
Rb_2O	(wt.%)	0.030	0	0
SrO	(wt.%)	0.018	0	0
ZrO_2	(wt.%)	0.056	0.005	0
MoO_3	(wt.%)	0	0.011	0

Fig. 12. Almus agates processed as jewelry and accessories

Rys. 12. Agaty Almus przetwarzane jako biżuteria i dodatki

Fig. 13. The answer to the question "why surprise egg"

Rys. 13. Odpowiedź na pytanie „po co jajko z niespodzianką"

Almus agates are surprise eggs of nature. Each sample contains a wide variety of color and texture combinations that are unique to them, which makes us wonder what kind of pattern and color palette will be encountered in each new agate. They are predominantly in droplet or spherical shape, reaching from mm to 25–30 cm, in a very large area.

It has been observed that the most important factors that make up the color and texture diversity in these agates are the forms of iron minerals and the elemental enrichment of iron within the individual chalcedony layers. Iron element enrichments (ca 1–1.5 wt.% Fe_2O_3), which are thought to be the most effective in fossil-like texture and color change formed by iron minerals, are the most important reason for making these agates rare and unique. In order to make the formation model of the Almus agates more understandable, the agates that have not yet completed their formation in the host rock and the completed agates are compared in Figure 14. As can be seen in Figure 14a, agates that have not yet completed their

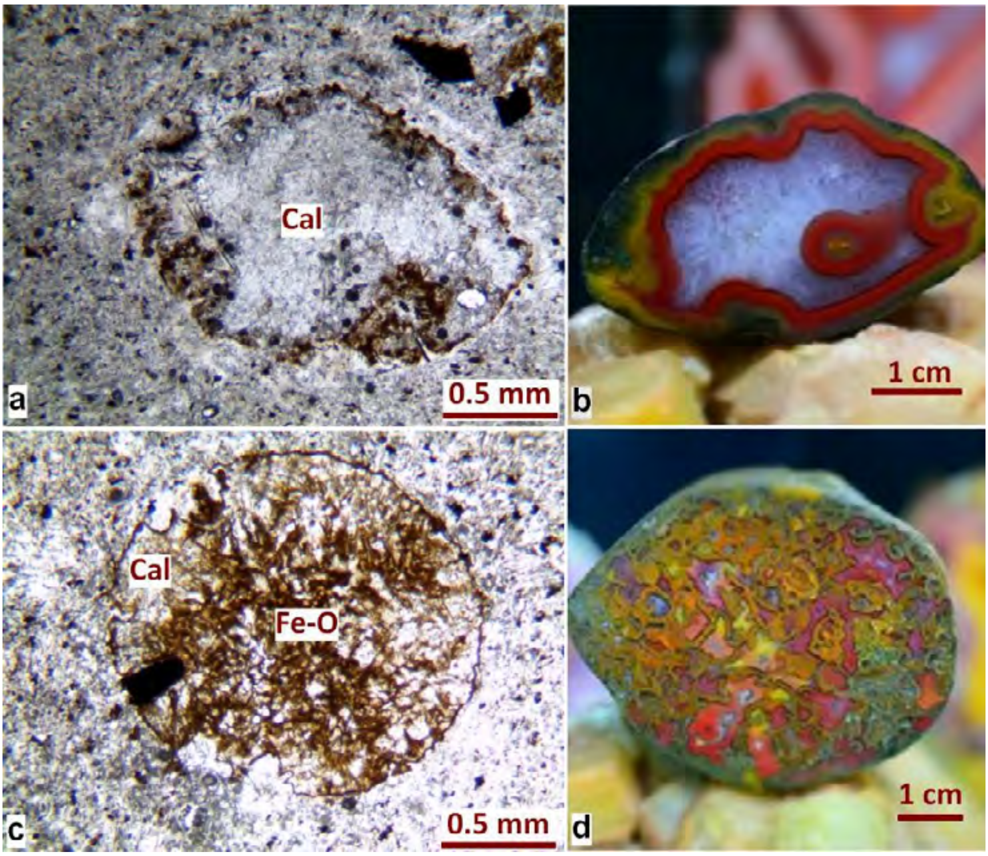

Fig. 14. Comparison of micro (a, c – thin section images) and macro (b, d – macro agate images) formations of Almus agates

Rys. 14. Porównanie formacji agatów Almus mikro (a, c – obrazy cienkich przekrojów) i makro (b, d – obrazy makroagatów) development in microvoids in the host rock contain iron oxide outside and calcite inside the nodule. In the macro agate sample found in Figure 14b, which completed its formation in a similar form, the outer parts turned into chalcedony in different tones rich in iron, and the inner parts turned into coarse crystalline quartz.

In Figure 14c, there is an example of agates that have not yet completed their development in the host rock and that contain intense iron-oxide formation and calcite as filling. The agates that complete their formation in these pores turn into agates as in Figure 14d. While the iron oxide here creates textures like fossil; microcrystalline quartz mineral zones in different color tones are formed instead of calcite mineral.

It is thought that Almus agates, which can be used as gemstone for reasons such as color and pattern variety, workability, polish retention and durability, can be a desirable product for agate lovers and collectors.

Some of the Almus agates taken from the study area were processed in Ümit Ulus gemstone shaping workshop and jewelry and accessory objects were produced. We thank Ümit ULUS for their assistance in processing and photographing the Almus agates.

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SURPRISE EGGS, THE MIRACLE OF NATURE: ALMUS AGATES (TOKAT – TURKİYE)

Keywords

agate, gemstone, mineralogy, gemology, geochemistry

Abstract

Almus agates which are forms of nodules like egg-shaped are located in the Eocene aged Almus volcanics in Tokat (Turkey). These nodules are surprise eggs in spherical or oval form ranging from a few cm to 25–30 cm. It is thought that the most effective reason for the formation of the magnificent texture and color combinations of the agates in the region is the iron element. In thin section studies, agate formations are composed of length-slow zebraic chalcedony and quart zine. In addition, curved fossil like structures composed of iron oxide minerals offer visual richness.

The host rock in which the Almus agates are located is trachyte, which consists of sanidine, plagioclase microlites and small opaque minerals, in which microlithic porphyritic and flow (trachytic) texture are observed. As a result of the multipoint eds (field emission scanning electron microscope), it was determined that the quartz is composed of Si, O and Fe. The content of the iron element, which is thought to cause color, was observed in the range of ca 1–1.5 wt.%. According to XRF analysis results, in Almus agates, there is depletion of Fe_2O_3 content in fine crystalline regions (ca 1 wt.%) compared to coarse crystalline zones (ca 1.5 wt.%).

In order to determine the usability of Almus agates as gemstone, various cabochon shapes were made in Ümit Ulus Gemstone Processing workshop. It has been observed that these agates can be used for both collection and gemstone purposes due to their unique patterns and color compensation.

JAJA NIESPODZIANKA, CUD NATURY: AGATY ALMUS (TOKAT – TURCJA)

Słowa kluczowe

agat, kamień jubilerski, mineralogia, gemologia, geochemia

Streszczenie

Agaty Almus, które mają formę guzków jajowatych i znajdują się w eoceńskich wulkanach Almus w Tokat (Turcja). Te guzki to jaja niespodzianki w kształcie kulistym lub owalnym, o wielkości od kilku do 25–30 cm. Uważa się, że najskuteczniejszym powodem powstawania wspaniałej faktury i kombinacji kolorów agatów w regionie jest pierwiastek żelaza. W badaniach cienkich przekrojów, formacje agatowe składają się z zebrowego chalcedonu i kwarcytu. Ponadto zakrzywione struktury przypominające skamieliny, złożone z minerałów tlenku żelaza, zapewniają wizualne bogactwo.

Skała macierzysta, w której znajdują się agaty Almus, to trachit, na który składają się sanidyna, mikrolity plagioklazowe oraz drobne minerały nieprzezroczyste, w których obserwuje się mikrolityczną teksturę porfirytową i przepływową (trachytyczną). W wyniku wielopunktowego EDS (skaningowego mikroskopu elektronowego z emisją polową) ustalono, że kwarc składa się z Si, O i Fe. Zaobserwowano zawartość pierwiastka żelaza, o którym sądzi się, że powoduje barwę, w zakresie od około 1 do 1,5% wag. Zgodnie z wynikami analizy XRF, w agatach Almus następuje zmniejszenie zawartości Fe_2O_3 w obszarach drobnokrystalicznych (około 1% wag.) w porównaniu do obszarów gruboziarnistych (około 1,5% wag.).

Aby określić przydatność agatów Almus jako kamieni szlachetnych, w pracowni Ümit Ulus Gemstone Processing wykonano różne kształty kaboszonów. Zaobserwowano, że te agaty mogą być używane zarówno do celów kolekcjonerskich, jak i kamieni szlachetnych ze względu na ich unikalne wzory i kompensację kolorów.