Mineralogical, geochemical and gemological investigation of Artova Ch-chalcedonies, Tokat – Turkey

Introduction

From the past to the present, natural stones have always been a part of our lives in human history. Natural Stones (Gözüpek 1996; Vieil et al. 2004; Hatipoğlu and Kırıkoğlu 2005; Hatipoğlu 2007) were used as functional tools such as axes, knives, gravestones in the first centuries, while in later periods, they were used in monuments and buildings that have survived for hundreds of years with the settling of humanity. At the same time, natural stones are used in jewelry and ornaments as well as the ones that have the charm, color, brightness and durability. At present, gemstones continue to take their place in our lives as an indispensable accessory. Anatolia is a region rich in quartz group gemstones with different colors and textures (Kaydu et al. 2018a, b, Başbüyük 2018). The Ch-chalcedonies, which are the subject of the study and rarely found in the world, are green colored quartz group gemstones (Krosch 1990; Shigley et al. 2009; Caucia et al. 2016; Lule-Whipp 2006; Hyrsl 2016).
Prasiolite, aventurine, chrysoprase and Ch-chalcedony are green colored members of the quartz group gem stones (Rossman 1994; Bank et al. 1997; Gercin 2005; Ayvacıklı et al. 2012). Prasiolite (Greek – leek-green stone) is a rare stone in nature. It can be produced artificially from violet amethyst or yellowish quartz by a combination of heat treatment and cobalt-60 or E-beam Gamma irradiation (https://www.gemdat.org). Aventurine is a form of quartz, characterised by its translucency and the presence of platy mineral inclusions as mica (fuchsite) and hematite that give a shimmering or glistening effect termed aventurescence (Korbel and Novak 1999). Ch-chalcedonies (Smith 1967; Hyrsl 1999) are very similar in color and texture to chrysoprases (Kinnunen and Malisa 1990; Nagase et al. 1997; Sojka et al. 2004; Hatipoğlu et al. 2011; Hatipoğlu and Yardımcı 2014), their difference from the chrysoprase is that they get their green color from the enrichment of Cr rather than Ni (Heflik et al. 1989; Sachanbinski et al. 2001; Willing and Stocklmayer 2003; Graetsch 2011). The Ch-chalcedony, which is the subject of the study, is found in the lacustrine dolomitic levels of Lower-Middle Eocene terrestrial clastics on the ophiolitic units in southwest of Tokat province in the North Anatolia region. Hydrothermal waters forming Ch-chalcedonies are thought to be enriched by the chromium element while passing through the ophiolites. In this study, it is aimed to determine paragenetic relations and mineralogical, geochemical and gemological characteristics of Ch-chalcedony in the study area.

1. Materials and methodology

Mineralogical determinations (mineral paragenesis) were made by examining the thin sections of the Cr-chalsedonies and side rocks taken from the area and prepared at Mersin University, Geological Engineering Department and the Thin Section Laboratory under polarizing microscope at Ahi Evran University Geological Engineering Mineralogy-Petrography Laboratory. In order to determine the mineralogical compositions of the samples, XRD analyses were carried out using Rigaku RadB-DMAX II Computer Controlled X-Ray Diffractometer and FT-IR analyses were carried out by means of Fourier-transform infrared spectroscopy of the Perkin Elmer Frontier model in the XRD Analysis Laboratory of Mersin University.

In order to determine the chemical composition of the samples, XRF extraction was performed with the use of Rigaku Marka (ZSX Primus II) X-ray fluorescence spectrometer at Mersin University Advanced Technology Education, Research and Application Center (MEITAM). The trace element analysis of the samples was carried out using the ICP/ICP-MS method in Acme Analytical Lab. (Canada).

In addition, Cabochon cutting techniques were used on Ch-chalcedony samples taken from the study area by using diamond coated saws, sintered diamond grinding discs and polishing machines to determine their usability as a gemstone.
2. Geology

The basement of the study area (Fig. 1) is composed of Permian-Triassic metamorphics consisting of: schist, phyllite, metabasite and marble (Akyazı 1991; Akyazı and Tunç 1992; Üstüntaş and İnceöz 1999). The Upper Jurassic – Lower Cretaceous pelagic limestones, neritic limestones and unconjugated basic, ultrabasic ophiolitic rocks unconformably overlie the Permo-Triassic clastics and carbonates (MTA 2002; Yılmaz and Yılmaz 2004; Tetiker 2010; Güreli Yolcu et al. 2014). Lower-Middle Eocene continental clastics and Quaternary alluviums unconformably cover all the units. Chromium chalcedony is in the form of veins and lenses which reach from several centimeters to about one meter thick in the dolomitic limestones in the Lower-Middle Eocene aged clastics-terrestrial levels.

Fig. 1. Geological map of the study area (MTA 2002)

Rys. 1. Mapa geologiczna badanego obszaru
3. Findings

3.1. Field studies

Grayish brown, light green/white-to-dark, green-colored Ch-chalcedonies in yellowish-white dolomitic limestones in the vicinity of the Ulusulu and Gümüşyurt Villages of Tokat province in northern Anatolia, consist of veins and lenses in cm-dm thickness (Fig. 2). Cuttings were made from Ch-chalcedonies of different colors and textures taken from the field in order to determine their thin section investigation and gemological characteristics (Fig. 3). The pale colors were observed on the outer surface of the samples, and when they were cut, it was observed that they had darker and lively colors.

Fig. 2. Ch-chalcedonies of varying colors ranging from light green to dark green in dolomitic limestone levels in the study area

Rys. 2. Ch-chalcedony o różnych kolorach, od jasnozielonego do ciemnozielonego na poziomach wapienia dolomitycznego w badanym obszarze
3.2. Mineralogical and petrographical investigations

In the petrographical investigations made of thin sections, Ch-chaledonies are generally composed of microcrystalline quartz (Fig. 4a, b); there are abundant micro-fractures and
Fig. 4. a–b – Micro-crystalline quartz minerals in the Ch-chalcedony sample (a: crossed polars, b: plane-polarized light), c–d–e – microcrystalline and fibrous quartz minerals in Ch-chalcedony, micro-fractures and cracks filled with opaque ore minerals (c: crossed polars, d: plane-polarized light, e: crossed polars), f – microfossils in dolomitic limestones and microcrystalline quartz in pore-cavities (crossed polars)

Rys. 4. a–b – Mikrokrystaliczne minerały kwarcu w próbie Ch-chalcedonu (a: skrzyżowane bieguny, b: światło spolaryzowane płasko), c–d–e – mikrokrystaliczne i włókniste minerały kwarcu w Ch-chalcedonach, mikropęknięcia i pęknięcia wypełnione nieprzezroczystymi mineralami rudy (c: skrzyżowane bieguny, d: światło spolaryzowane płasko, e: skrzyżowane bieguny), f – mikroskamieliny w wapieniach dolomitycznych i mikrokrystaliczny kwarc w zagłębieniach porów (skrzyżowane bieguny)
cracks in it; these fractures and cracks are filled with opaque secondary iron oxide and/or ore minerals (Fig. 4c, d). At the same time, Ch-chalcedonies contain some fibrous needle-like levels and coarse crystalline levels (Fig. 4e). Micritic dolomitic limestone, contains plenty of micro-fossils and microcrystalline quartz in pores and cavities (Fig. 4f).

### 3.3. XRD and FT-IR Investigations

In order to determine the mineral contents of the rock samples taken from the study area, XRD and FTIR shots of the samples taken from Ch-chalcedony and side rock in different colors and textures were made. According to the results of XRD and FTIR analyses, Ch-chalcedonies are generally composed of quartz only; in some samples, quartz is accompanied by cristobalite, tridymite and cuspidine minerals (Figs 5–6). The dolomitic limestones forming the host rock are composed of dolomite minerals (Fig. 7).
Fig. 6. FTIR shots of Ch-chalcedony samples

Rys. 6. Zdjęcia FTIR próbek Ch-chalcedonu

Fig. 7. XRD diffractogram of the host rock of Ch-chalcedony

Rys. 7. Dyfraktogram XRD skały macierzystej Ch-chalcedonu
3.4. Geochemical investigations

The results of the main element analysis of Ch-chalcedony samples taken from the study area are given in Table 1. The main oxide percentages in the samples were measured as \( \text{SiO}_2 \) 95.86–97.81, \( \text{Al}_2\text{O}_3 \) 0.04–0.29, \( \text{Fe}_2\text{O}_3 \) 0.61–0.91, \( \text{MgO} \) 0.07–0.82, \( \text{CaO} \) 0.02–0.18, \( \text{Na}_2\text{O} \) 0.01–0.07, \( \text{K}_2\text{O} \) 0.01–0.04, \( \text{TiO}_2 \leq 0.01, \text{P}_2\text{O}_5 \leq 0.01, \text{MnO} \leq 0.01, \text{Cr}_2\text{O}_3 \) 0.125–0.168. Results of trace element analysis of Ch-chalcedony samples taken from the study area are given in Table 2. In Ch-chalcedonies, significant enrichments are observed in: Mo, Cu, Ni, Mn, V, Cr and W, especially in Cr, these enrichments are up to 705 ppm. Regarding trace element content of the dolomitic limestones in which Ch-chalcedonies are found, significant enrichments are observed in Cu, Ni, Mn, V and Cr, similarly to Ch-chalcedony.

Table 1. Results of XRF main oxide analysis of Ch-chalcedony and host rock samples

<table>
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<tr>
<th>Sample number</th>
<th>Chromatic Chalcedony</th>
<th>Dolomite</th>
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<tbody>
<tr>
<td>SiO₂</td>
<td>97.42</td>
<td>97.81</td>
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<tr>
<td>Al₂O₃</td>
<td>0.07</td>
<td>0.04</td>
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<tr>
<td>Fe₂O₃</td>
<td>0.61</td>
<td>0.91</td>
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<td>MgO</td>
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<tr>
<td>CaO</td>
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<td>0.03</td>
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<tr>
<td>Na₂O</td>
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<tr>
<td>K₂O</td>
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<td>0.01</td>
</tr>
<tr>
<td>TiO₂</td>
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<td>&lt;0.01</td>
</tr>
<tr>
<td>P₂O₅</td>
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</tr>
<tr>
<td>MnO</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>Cr₂O₃</td>
<td>0.132</td>
<td>0.168</td>
</tr>
<tr>
<td>LOI</td>
<td>1.4</td>
<td>1.1</td>
</tr>
<tr>
<td>Total</td>
<td>100.03</td>
<td>100.02</td>
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Table 2. ICP-MS trace element analysis results of Ch-chalcedony and host rock samples

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<td></td>
<td>TK-2</td>
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<tr>
<td>Mo</td>
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<td>Cu</td>
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<td>Pb</td>
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<tr>
<td>Ag</td>
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<td>Ba</td>
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<tr>
<td>W</td>
<td>2.2</td>
<td>2.6</td>
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<td>&lt;0.01</td>
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<td>0.1</td>
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<tr>
<td>Ti</td>
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<td>&lt;0.1</td>
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<tr>
<td>Ga</td>
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<td>&lt;0.5</td>
</tr>
<tr>
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<td>&lt;0.2</td>
</tr>
<tr>
<td>Zr</td>
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<tr>
<td>Y</td>
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<td>&lt;3</td>
</tr>
<tr>
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</tr>
<tr>
<td>Sc</td>
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</tr>
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</table>
3.5. Gemological investigations

The Ch-chaledonies, which are rarely found in the world, have a great potential reserves in the study area. The varying colors from brownish gray and light green to dark green of Ch-chaledonies are the most prominent feature in its use as a gem stone. The hardness, the high gain and good polishing resistance of the Ch-chaledonies, which is member of quartz group gemstones, are the other characteristics which allows the use as gemstones.

In order to determine the usability of Ch-chaledonies as gem stones, 8 mm slices were taken to make the cabochon from the samples taken from the study area (Fig. 8a). The circle, oval and drop shapes are marked on the slices with the help of stencils and a steel pen. Ch-chaledony, which was processed as a cabochon, was abraded with silicon carbide abrasive powder on the metal disc in the horizontal lab machine, then polished with cerium oxide polish powder on the felt coated disc and the final products were made ready for use in the jewelry (Fig. 8b, c, d). It is envisaged that Ch-chaledony may be used as the gem stone when considering the color, texture, brightness of the products obtained, taken large size parts from the study area and the largeness of the possible reserves.

Results

Ch-chaledonies are present within the Lower-Middle Eocene aged dolomitic limestones as veins and lenses from several cm to one meter thick in the study area in the North
Anatolian region. Ch-chalcedonies in brownish gray, light green to dark green color have a great possible reserve in the study area.

According to results of thin section analysis of Ch-chalcedonies, they are generally composed of microcrystalline quartz, where there are coarse crystalline levels in places, and there are plenty of micro-fractures and cracks. These fractures and cracks are filled with opaque secondary iron oxide and/or ore minerals. For this reason, Ch-chalcedony has a cloudy dull appearance and does not have any transparency.

According to the results of XRD and FTIR analysis, Ch-chalcedonies are generally composed of the quartz mineral, but in some samples quartz is accompanied by crystals of cristobalite, tridimite and cuspidine.

According to the chemical analysis of Ch-chalcedony samples, the main oxide percentages were measured as: SiO$_2$ 95.86–97.81, Al$_2$O$_3$ 0.04–0.29, Fe$_2$O$_3$ 0.61–0.91, MgO 0.07–0.82, CaO 0.02–0.18, Na$_2$O 0.01–0.07, K$_2$O 0.01–0.04, TiO$_2$ ≤ 0.01, P$_2$O$_5$ ≤ 0.01, MnO ≤ 0.01, Cr$_2$O$_3$ 0.125–0.168. As expected, Ch-chalcedony samples have enrichments in the amounts of Fe$_2$O$_3$ and Cr$_2$O$_3$. According to trace element analysis results, significant enrichments in: Mo, Cu, Ni, Mn, V, Cr and W were observed in Ch-chalcedonies. In the trace element content of the dolomitic limestones in which Ch-chalcedonies are found, significant enrichments are observed in Cu, Ni, Mn, V and Cr, similarly to Ch-chalcedony. The origin of these enrichments in dolomitic limestones is thought to be the hydrothermal source of Ch-chalcedony. Assuming that the hydrothermal system, which provides enrichment in the metallic ore elements within the dolomitic limestones and Ch-chalcedonies, is the same, it is considered as an interesting result that Cr in Ch-chalcedony (Cr: 489–705 ppm) is about 4–5 times higher than in the dolomitic limestones (Cr: 131 ppm) and Ni in Ch-chalcedony (Ni: 9.4–23.2 ppm) is about 5–11 times lower than in the dolomitic limestones (Ni: 105 ppm). This situation suggests that the reason of the enrichment of Cr instead of Ni during the formation of green colored gem stones is not caused by the elemental content of the hydrothermal system. The answer to the question of what could be the mechanism causing the enrichment of Cr instead of Ni in Ch-chalcedonies structures, is expected to be solved in the next studies.

Ch-chalcedonies in the study area can be used as gem stone due to its characteristics such as: color, durability, low macro-fracture, easy processing and polishing. The Ch-chalcedony is suitable for small-size jewelry production as well as for the production of large-scale ornaments due to the size of the veins reaching 1 m thick in the study area.

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REFERENCES

MTA 2002. 1/500.000 scale geological map of Turkey, General Directorate of Mineral Research and Exploration, Ankara.
Ch-chalcedony is a green colored member of the quartz group of gem stones. The appearance of Ch-chalcedony is very similar to that of chrysoprase. Differently, Ch-chalcedonies have a chromium element instead of a nickel element as a trace element. Green quartz used in jewelery as a seal stone, in necklaces and rings and has been one of the most valuable quartz varieties throughout history, with its beautiful green color, more rare than other quartz varieties.

The Ch-chalcedonies in the North Anatolian region is yellowish-white, brownish gray, light green to dark green in color ranging from several centimeters to one meter thick in veins and lenses in the Lower-Middle Eocene dolomitic limestones. Ch-chalcedonies are composed of fine-grained and occasionally fibrous needle-like quartz; in some examples, quartz is present together with cristobalite, tridimite and cuspidine minerals. According to geochemical investigations in Ch-chalcedonies, the main oxides that were determined are as follows: $\text{SiO}_2$ was observed in the range of 95.86–97.81%, $\text{Fe}_2\text{O}_3$...
was observed in the range of 0.61–0.91% and Cr₂O₃ was observed in the range of 0.125–0.168%. A trace element analysis of Ch-chalcedonies, shows their significant enrichments in: Ni, Mo, Cu, Mn, V, Cr and W, especially in the Cr (up to 705 ppm). The green color of the studied Cr-chalcedonies originates from the element chromium. Taking the possible reserves into account, the hardness, color, massive structures, mineralogical, petrographical and gemological features of Ch-chalcedonies in the region are evaluated together. It is determined that they are suitable for the production of jewelry and ornaments.

MINERALOGICZNE, GEOCHEMICZNE I GEMOLOGICZNE BADANIA CH-CHALCEDONÓW Z ARTÓWA, TOKAT – TURCJA

Słowa kluczowe

Ch-chalcedon, kamień szlachetny, zielony kwarc, gemologia, Turcja

Streszczenie

Ch-chalcedon jest składnikiem kwarcowej grupy kamieni szlachetnych w kolorze zielonym. Wygląd Ch-chalcedonu jest bardzo podobny do chryzoprazu. W szczególności Ch-chalcedony zawierają pierwiastek chromu zamiast pierwiastka niklu jako pierwiastka śladowego. Zielony kwarc stosowany w biżuterii jako kamień do: pieczętowania, naszyjników i pierścionków był jedną z najcenniejszych odmian kwarcu w historii dziejów.

Ch-chalcedony w regionie północnoatlantyckim mają żółtawo-biały, brązowo-szary kolor od jasnozielonego do ciemnozielonego o grubości od kilku centymetrów do jednego metra, występują w żyłach i soczewkach wapieni dolomitycznych dolno-środkowego eocenu. Ch-chalcedony składają się z drobnoziarnistego i czasami włóknistego igłopodobnego kwarcu; w niektórych próbkach kwarc występuje razem z minerałami krystobalitu, tridymitu i kuspidyny. Według badań geochemicznych w Ch-chalcedonach zawartość głównych tlenków kształtowała się następująco: SiO₂ zaobserwowano w zakresie 95,86–97,81%, Fe₂O₃ zaobserwowano w zakresie 0,61–0,91%, a Cr₂O₃ zaobserwowano w zakresie 0,125–0,168%. Analiza pierwiastków śladowych Ch-chalcedonów pokazuje ich znaczące wzbogacenie w: Ni, Mo, Cu, Mn, V, Cr i W, szczególnie w Cr (do 705 ppm). Zielony kolor badanych Ch-chalcedonów pochodzi od pierwiastka chromu. Obecnie oceniane są: możliwe zasoby, twardość, kolor, struktury, cechy mineralogiczne, petrograficzne i gemologiczne chalcedonów w analizowanym regionie. Ustalono, że te Ch-chalcedony nadają się do produkcji biżuterii i ozdób.