



Mineralogical, geochemical, and gemological characteristics of silicic gemstone in Aydıncık (Yozgat-Turkey)

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Abstract

There are chalcedony and amethyst formations in two fields in Aydıncık-Yozgat (West of Aydıncık District, Keşlik area and Southwestern of Hacıilyas). The gemstones in this region have been formed within the gaps and cracks of the brecciated rocks of the fault zone in altered andesites. Chalcedony and amethyst are either present in the form of crack fillings from a few millimeters to 10 cm in width, or in the form of generally oval pore fillings reaching a few centimeters to 40 cm in diameter. The chalcedony is composed of 0.1-mm–centimeter-thick bands parallel to each other in varying tones ranging from light blue/white to dark blue to reddish brown, and in some points in the central part of this banded structure are large crystalline quartz and amethysts. Chalcedony occurs as kidney–banded and geodesic forms as cryptocrystalline and macrocrystalline. The altered volcanic rock with brecciated texture, which hosts chalcedony and amethyst occurrences in both regions, is the altered andesite. Petrographic examinations carried out from chalcedony and amethysts indicated that gemstones composed of fine-coarse grained quartz have microcrystalline texture in the rim zones and have macrocrystalline texture toward the core. XRD analysis of chalcedony and amethyst with different colors and crystal grain sizes revealed that gemstones in the region were composed of large and microcrystalline quartz. When amethyst, blue chalcedony, and reddish brown chalcedony were compared to white transparent quartz, there was a significant increase in the amounts of Fe_2O_3 and Al_2O_3 , and metal elements (Mo, Cu, Pb, Zn, Ni, Co, Mn, Cr) in the case of amethyst and reddish brown chalcedony. The visible reserves of chalcedony and amethysts in the region, their dimensions and varying color range, and large-grained texture and physical properties show that the chalcedonies and amethyst formations can be used as gemstones. Use of these formations as gemstones also makes a significant contribution to the regional economy.

Keywords Gemology · Geochemistry · Chalcedony · Amethyst · Gemstone

Introduction

There are 11 major basins in central Anatolia—the Haymana, Çankiri, Kirikkale, Tuzgözü (s.s), Ulukışla, Şarkışla, Refahiye, Sivas, Yıldızeli, Yozgat-Sorgun, and Kırşehir-Kaman (Görür et al. 1998). The study area is located in the Yozgat-Sorgun Basin. The Yozgat-Sorgun Basin extends along the southern side of the Ankara-Erzincan suture between the cities of Yozgat and Sorgun

(Görür et al. 1998). The Yozgat-Sorgun Basin formed during the Eocene and accumulated thick turbidites during Ypresian through Lutetian time (Görür et al. 1998). Within the Lutetian section, volcanic and volcanoclastic rocks, including basalt, andesite, agglomerate, and tuff horizons, are locally abundant (Görür et al. 1998). After the Lutetian, the Yozgat-Sorgun Basin was folded and uplifted (Görür et al. 1998). Terrestrial sedimentation with conglomerates, sandstones, evaporites, and local lacustrine limestones commenced in the early Miocene and lasted, with some volcanism, into Pliocene time and to the present day (Görür et al. 1998).

The Central Anatolian Region, which includes the area of investigation, has plenty of chalcedony and amethyst formations in different colors and textures. Eskişehir (Hatipoğlu et al. 2013), Ankara (Hatipoğlu and Dora

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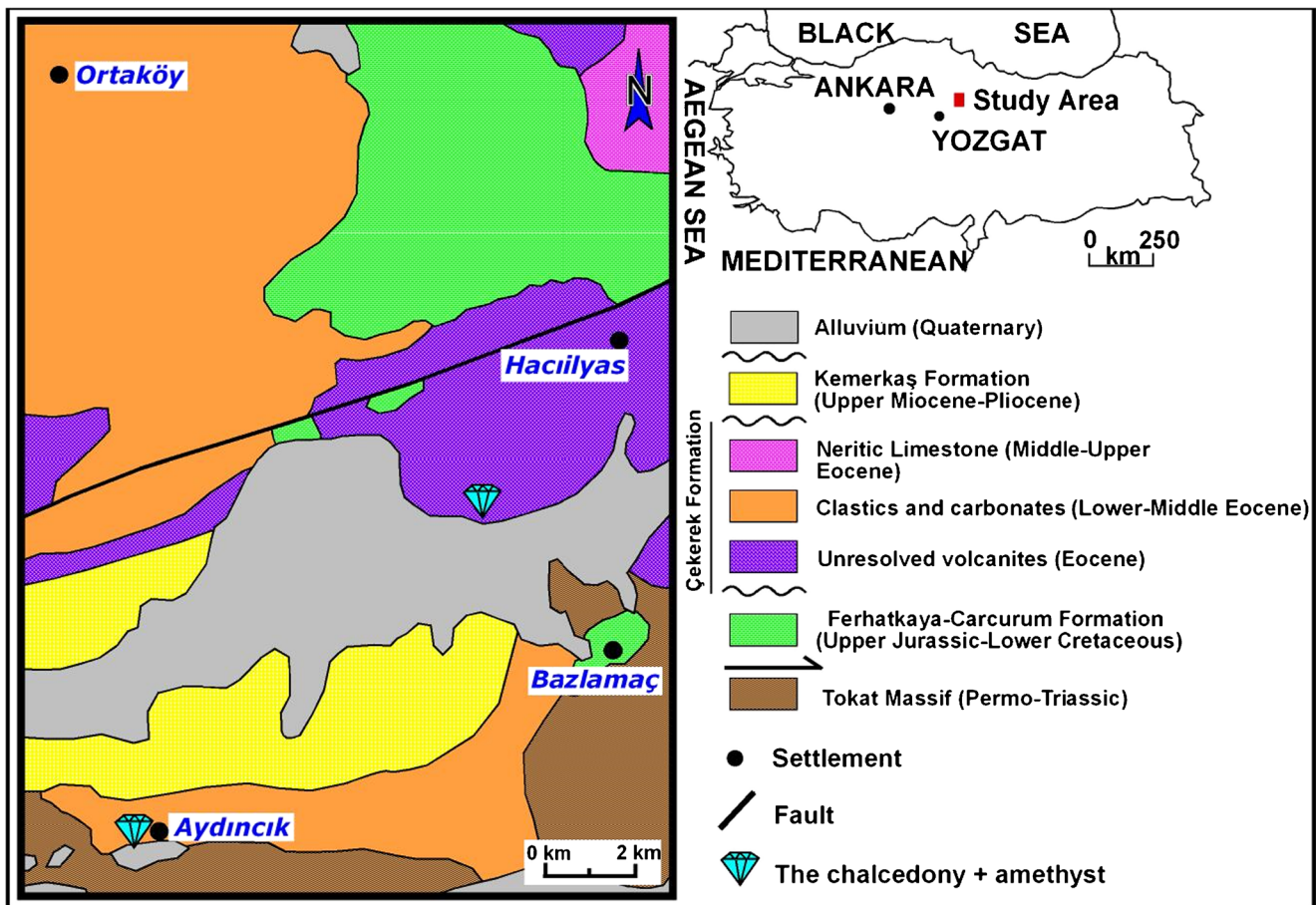


Fig. 1 Geological map of the area of investigation (MTA 2002; Akbudak et al. 2018)

2000), and Yozgat (Çevik and Sayılı 2010) cities are the richest regions in Anatolia in terms of siliceous gemstones (chalcedony, amethyst, rose quartz, etc.). The blue chalcedony and rarely found amethysts commonly observed in the silicic gemstones have been formed in the gaps and cracks of the breccias in the altered andesites in the area of investigation. These chalcedonies and amethysts, which are composed of approximately 94–99% silica and oxygen as the main element, are widely used in jewelry and souvenir production as a gemstone in the stone processing workshop established by the Aydınçık Public

Training Center (Akbudak et al. 2018). These gemstone formations have similar characteristics with the chalcedony and amethyst formations found in Yozgat-Yerköy-Belkavak village (Çevik 2009; Çevik and Sayılı 2010). The main objective of this study is to determine the geochemical and gemological characteristics of the siliceous gemstones with different colors and textures found in the investigation.

Amethyst is a violet or violet-colored quartz mineral. This color occurs when silicon atoms are replaced by iron atoms (Barry and Moore 1964; Adekeye and Cohen 1986;

Fig. 2 Blue chalcedony formations (a, b) that develop within the brecciated level in the altered volcanic rocks in the southwestern part of Hacılıyas town (Akbudak et al. 2018)

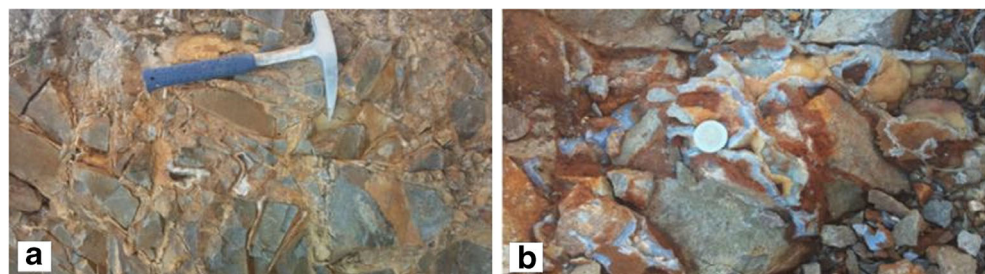
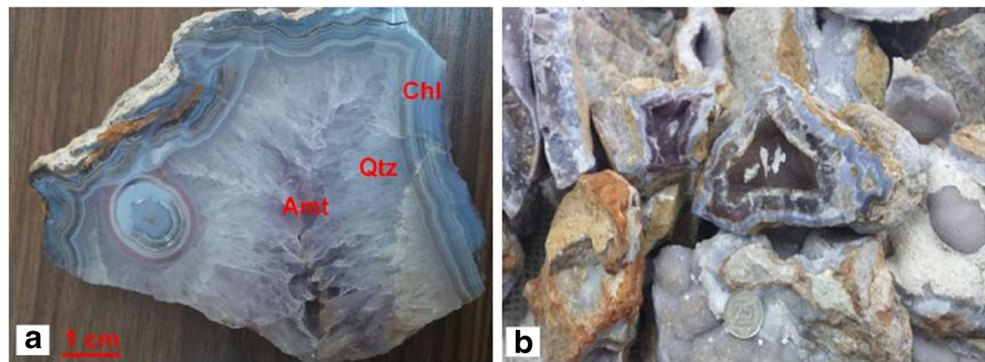


Fig. 3 Chalcedonies and amethysts with different colors and textures (a, b) in the southwestern part of Hacılıyas town (Akbulduk et al. 2018)



Kumbasar and Aykol 1993; Balitsky et al. 2000). The results of chemical analysis carried out on the amethysts from the study area demonstrate that aluminum elements along with the iron replace the silicon atoms in the crystal structure. Chalcedony mineral is one of the cryptocrystalline varieties of quartz minerals (Fronde1 1978, 1982). It has a greasy brilliance. Pure chalcedony consists of very thin quartz fibers aligned in very thin layers (Flörke et al. 1983, 1991; Gislason et al. 1993; Graetsch 1994). The pure calcium is semi-transparent gray or white. There are also grayish blue or brownish shaded and even blackish colors. Specific gravity is between 2.59 and 2.61 g/cm³ and different colors and patterns develop in the strips due to impurities (Hatipoğlu et al. 2010a, b; Selim 2014). The dominant texture of the chalcedonies in the region is blue tones and reddish browns are visible as well. While no significant change was observed in the main oxides in the blue and transparent specimens, an increase was found in the amount of iron in the reddish brown specimens.

Material and method

Forty-five specimens were taken from the area of the study with the aim of determining the distribution, paragenetic relationships, and mineralogical-petrographic, geochemical, and gemological characteristics of the chalcedony and amethysts under investigation (Akbulduk et al. 2016). Thin sections were prepared from chalcedonies,

amethysts, and wall rocks taken from the land at Mersin University Geological Engineering Department—Thin Section Laboratory. Mineralogical determinations (mineral paragenesis) were carried out by examining thin sections at the Ahi Evran University Geological Engineering Mineralogy-Petrography Laboratory by using an underground illuminated polarizing microscope. XRD analyses were carried out at the Mersin University XRD Analysis Laboratory by a Rigaku RadB-DMAX II computer-controlled X-ray diffractometer (CuK α , 30 kV, 15 mA, $\lambda = 0.154051$ nm) with the aim of identifying the mineralogical compositions of the specimens. The major and trace/trace element analyses of the specimen were carried out by Acme Analytical Lab. Speed. Ltd. Company (Acme) in Canada by the XRF and ICP/ICP-MS methods.

Geology

The geological map of the study area was drawn by rearranging the geological map of MTA (Mineral Research and Exploration Institute) (2002) (Fig. 1). Chalcedony and amethysts were formed in the altered Eocene volcanics of the Çekerek Formation (Akbulduk et al. 2018).

The oldest unit in the area of investigation is the Permo-Triassic Tokat Massive. The unit is represented by marble, metavolcanites, meta-sedimentary, and mica-schists (Üstündağ and İnceöz 1999; Özsert 2009). The Late Jura-

Fig. 4 The alternation of the laminae consisting of quartz (Qtz (Kretz 1983)), microcrystalline quartz (M-Qtz), and fibrous/acicular quartz (F-Qtz) minerals in the calcedon sample plane-polarized light (a) and cross-polarized light (b) image (Akbulduk et al. 2018)

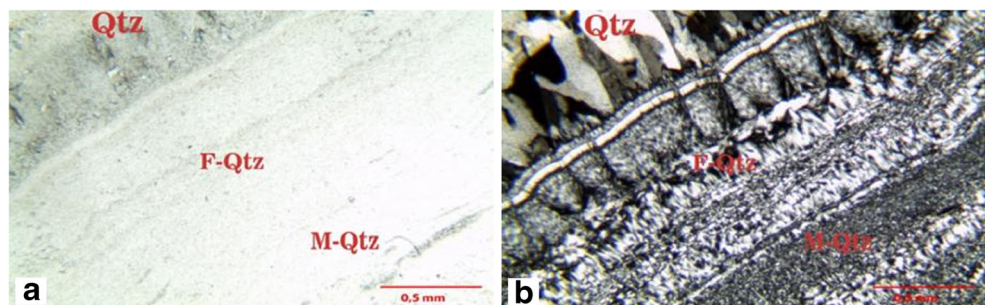
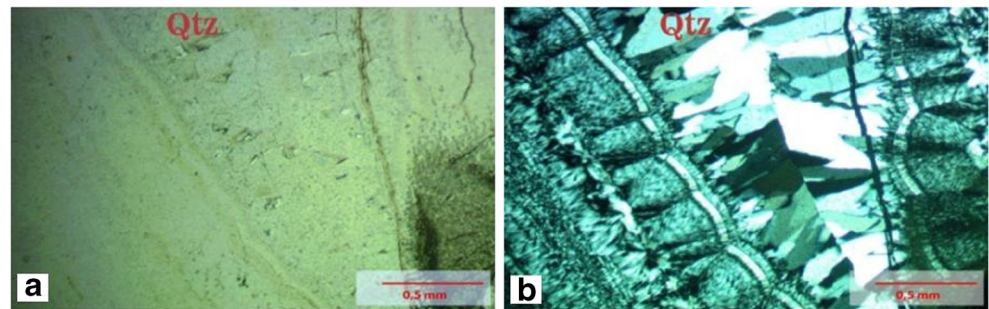


Fig. 5 Quartz with dovetail twinning, single nicol (**a**) and double nicol (**b**) image of the fibrous/acicular-microcrystalline at the edges and macrocrystalline quartz at the center (Akbuldak et al. 2018)



Early Cretaceous age Ferhatkaya and Carcurum Formations begin with a thin conglomerate level made of metamorphic materials. The formation is dominantly made up of limestones except the base. Common oolitic and pseudo-oolitic tissue and brecciated tissue are present in some places (Üstündağ and İnceöz 1999; Özsert 2009). The Carcurum Formation is generally composed of limestones and mudstone at the bottom and of limestones containing chert layers and lenses through the top (Üstündağ and İnceöz 1999; Özsert 2009). Eocene-aged Çekerek formation consists of a matrix formed by volcanic materials in general and unsegmented volcanics that contains agglomerate levels composed of basalt and andesite gravels and blocks in this matrix and mainly of pebble stone, sandstone, mudstone, claystone, marl, and limestone with abundant nummulite fossils in some levels from top to bottom (Üstündağ and İnceöz 1999; Özsert 2009). Within the unit, silicified wood fossils, metamorphic rock fragments,

recrystallized limestone and limestone blocks, mudstone and claystone pellets, and coal veins are observed (Üstündağ and İnceöz 1999; Özsert 2009). The Upper Miocene-Paleocene-aged Kemerkaş formation overlain Çekerek formation with a discordant contact consists of conglomerate, pebble, coarse sandstone alternation, mudstone, gypsum-intercalated layers, and travertine (Üstündağ and İnceöz 1999; Özsert 2009). Quaternary-aged alluviums come discordantly on all these units.

Findings

Field study

The field study results showed that the two gemstone formations in the investigation area Figwere both within

Fig. 6 XRD analysis of siliceous gemstones with different colors and textures in the area of investigation (Akbuldak et al. 2018)

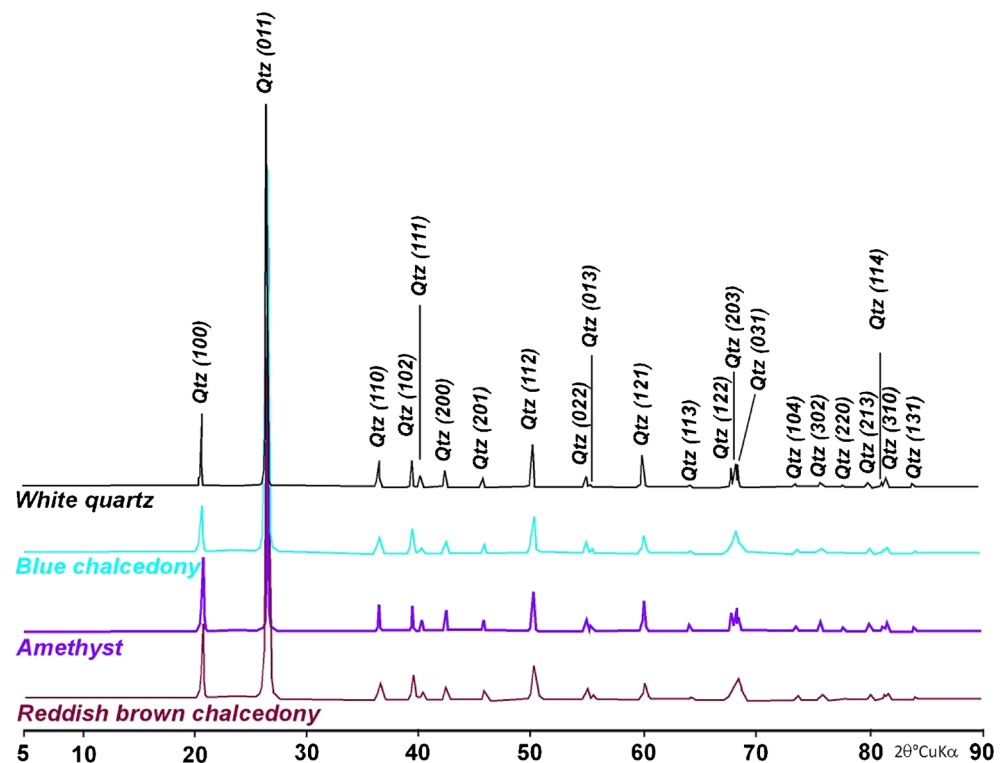
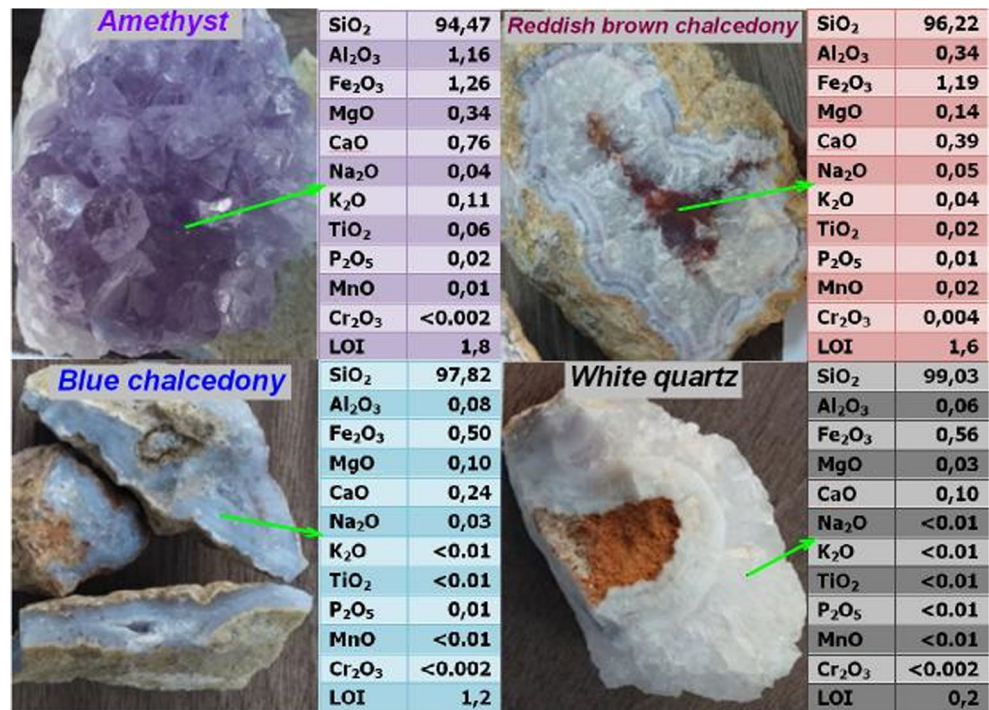


Fig. 7 The major element contents (wt%) of the silicic gemstones with different colors and textures in the area of investigation



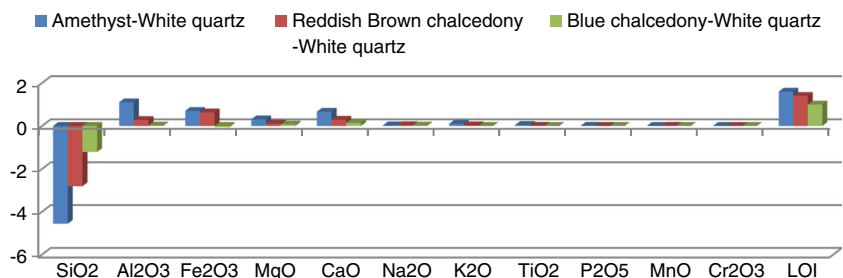
a brecciated zone reaching about a hundred meters in width and several hundred meters in length in altered andesites (Fig. 2a). Chalcedonies and amethysts in the southwestern part of the Hacılıyas region are found in the form of crack fillings reaching from a few millimeters to 10 cm or pore fillings reaching from a few centimeters to one and a half meters in diameter (Fig. 2b). The chalcedonies encompass 0.1-mm–cm bands parallel to each other in varying tones ranging from light blue/white to dark blue to brownish red, and the central part of this banded structure is composed of chalcedonies and amethysts containing large crystal quartz minerals (Fig. 3a). Gemstones found in this area have a larger reserve than the western part of Aydıncık Keşlik location, and the vein thickness and pore sizes are also bigger. At the same time, the color variation is also rich. In some specimens, kidney and banded structures and geode formations were also observed (Fig. 3b) (Akbulduk et al. 2018).

Mineralogical-petrographical investigations

The rock, which houses the chalcedony and amethyst formations in both regions, is altered andesite with hypo-crystalline hypidiomorphic porphyric texture and plagioclase + amphibole mineral paragenesis as the phenocrystal. Quartz phenocrystal + quartz microcrystal + fibrous/pearl-quartz were detected in petrographic examinations made from thin sections of chalcedony and amethyst (Fig. 4). Quartz on which dovetail twinning was seen were observed to be microcrystalline at the edges and to be macrocrystalline through the center (Fig. 5). There are also spherical textures formed by radially aligned fibrous/acicular quartz minerals in some places from the center to the edge (Akbulduk et al. 2018).

In XRD analysis made from white quartz, amethyst, and blue and reddish brown chalcedony samples with different colors and textures, it was seen that all samples were completely of quartz (Fig. 6) (Akbulduk et al. 2018).

Fig. 8 Amounts of percentage change of amethyst, blue chalcedony, and reddish brown chalcedony compared to pure white quartz in the main oxides



Geochemical investigations

The major element contents of siliceous gemstones with different colors and textures are given in Fig. 7. When the amethyst, blue chalcedonies, and reddish brown chalcedonies are compared to pure white quartz, the percent amount change in the main oxides (Fig. 8) is observed: a significant decrease in the amount of SiO₂ and increase in the amount of Al₂O₃, Fe₂O₃, MgO, and CaO. When the amethyst, blue chalcedony, and reddish brown chalcedony are normalized to pure white quartz, the proportional amounts of percent amount change in the main oxides (Fig. 9) are observed as follows: In amethysts, increase of about 20 times in the amount of Al₂O₃ and about 10 times in the amount of MgO and K₂O; in blue chalcedonies, no significant change was observed in the main oxides; in reddish brown chalcedonies, increase of about 5 times in the amount of Al₂O₃, MgO, and Na₂O.

The trace element contents of siliceous gemstones with different colors and textures are given in Table 1. When the amethyst, blue chalcedony, and reddish brown chalcedony were compared to pure white quartz, trace element ppm changes were observed as follows: In amethyst and reddish brown chalcedony, enrichment of Sr, Ba, Pb, Cu, Cr, V, Zn, and Mn elements and decrease of Zr element; in blue chalcedony, decrease of Ba, Pb, Zn, and As and significant enrichment of Zr and Mn elements (Fig. 10). When the amethyst, blue chalcedony, and reddish brown chalcedony are normalized to pure white quartz, the proportional amounts of ppm change in the trace elements are observed as follows: In amethysts, increase of about 3–11 times in the amount of Sr, Cu, Co, Sc, V, Mn, and Th; in reddish brown chalcedony, increase of about 2–11 times in the amount of Sr, Mo, Cu, Cr, Sc, and Mn; in blue chalcedony, increase of about 9 times in the amount of Zr element (Fig. 11).

Gemological investigations

Chalcedonies and amethysts observed in the field of study have economic value that can be used as jewelry and

gemstone when they are evaluated in terms of their visible reserve, color content and continuity, mineral combination, and purity and textural properties on the field. Chalcedonies and amethysts, which have already been extracted from the field of study, are used in the stone processing workshops established by the Aydıncık Public Education Center for the production of jewelry and souvenirs.

Cabochon cutting in different sizes and sanding and polishing processes were applied to the chalcedony and amethysts with different colors and textures taken from the field of investigation. The processed gemstones were used in ornaments such as necklaces, rings, earrings, bracelets, brooches, key holders, and table top name badges (Figs. 12, 13, 14, 15, 16). The rich color spectrum of the chalcedonies in the region, their purity, stiffness, resistance to acid and atmospheric conditions, durability, varnishing capacity, reflection of light, and many other qualities demonstrate that these stones can be used as jewelry and gemstones.

Results and discussion

The semi-precious gemstone formations found in the area of investigation are outcropped in the West of Aydıncık Keşlik location and southwestern part of Hacıilyas. The gemstones in both regions have been formed in the gaps and cracks within the breccias developed in the fault/fracture zone in the altered andesites. They are small in size and are in the form of a crack filling reaching from a few centimeters to about 10 cm in size or pore fillings reaching from a few centimeters to one and half centimeters in diameter. Due to these formations in the region, amethyst and chalcedony raw materials are obtained in different dimensions. Large-sized silicic gemstones are used for making accessories such as nameplates, while small size silicic gemstones are used for making accessories such as rings, necklaces, and bracelets.

While there is no clear data about the origin of the water forming the gemstones of the area of investigation, the study

Fig. 9 Amounts of proportional change of amethyst, blue chalcedony, and reddish brown chalcedony normalized to pure white quartz in the main oxides

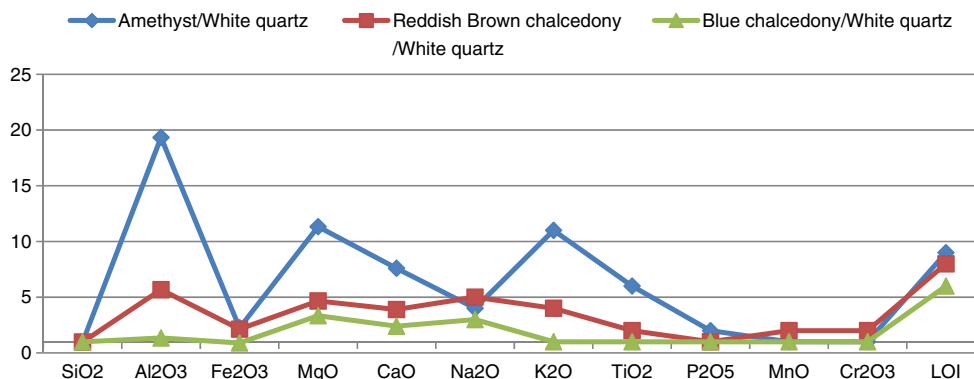


Table 1 Trace element contents (ppm) of silicic gemstones with different colors and textures in the area of investigation

Trace Elements		Amethyst	Reddish Brown chalcedony	Blue chalcedony	White quartz
Alkaline Earth Metal (AEM)	Sr	30	18	6	5
	Ba	73	69	27	36
Basic Metal (BM)	Bi	<0.1	<0.1	<0.1	<0.1
	Pb	80.2	98.4	40.1	55.2
	Tl	<0.1	<0.1	<0.1	<0.1
Transition Metal (TM)	Ga	<1	<1	<1	<1
	Mo	3.6	5.5	2	2.7
	Cu	11.6	9.9	3.5	3.9
	Zr	9	8	350	40
	Y	<3	<3	<3	<3
	Nb	<5	<5	<5	<5
	Cr	4	22	2	2
	Ni	4.6	5.7	2.1	2.1
	Co	2.8	1.5	0.7	0.5
	Sc	1.1	0.4	0.2	<0.1
	V	13	4	<2	<2
	Zn	51	59	21	28
	Mn	107	111	44	25
	Cd	<0.1	0.1	<0.1	0.1
Semimetal (S)	W	<0.1	0.3	0.1	0.2
	Hg	<0.01	<0.01	<0.01	<0.01
	As	15.5	43.1	13.6	24.9
	B	<20	<20	<20	<20
	Te	<0.2	<0.2	<0.2	<0.2
Precious Metal (PM)	Sb	0.1	0.3	<0.1	0.2
	Ag	<0.1	0.2	<0.1	<0.1
Nonmetal (N)	Au	0.0064	0.007	0.0045	0.0066
	Se	<0.5	<0.5	<0.5	<0.5
Lanthanide (L)	La	2	<1	<1	<1
Actinide (A)	Th	0.3	0.1	<0.1	<0.1

conducted by Çevik and ve Sayılı (2010) on the quartz and amethyst formations close to the region reported that the temperatures measured in white quartz were between 272 and

323 °C and the salinity was between 3.86 and 4.65% NaCl. The study also determined that at the transparent quartz-I phase, temperatures were between 217 and 280 °C, and

Fig. 10 Amounts of ppm changes of amethyst, blue chalcedony, and reddish brown chalcedony in trace elements compared to pure white quartz

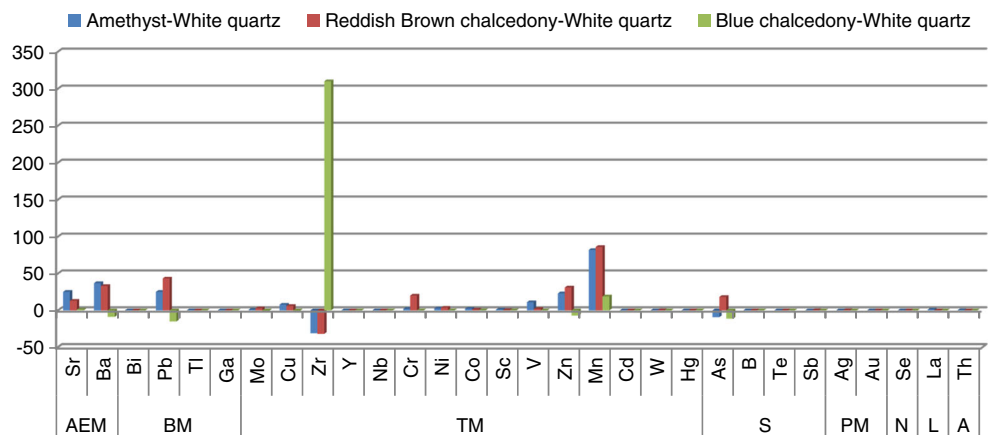
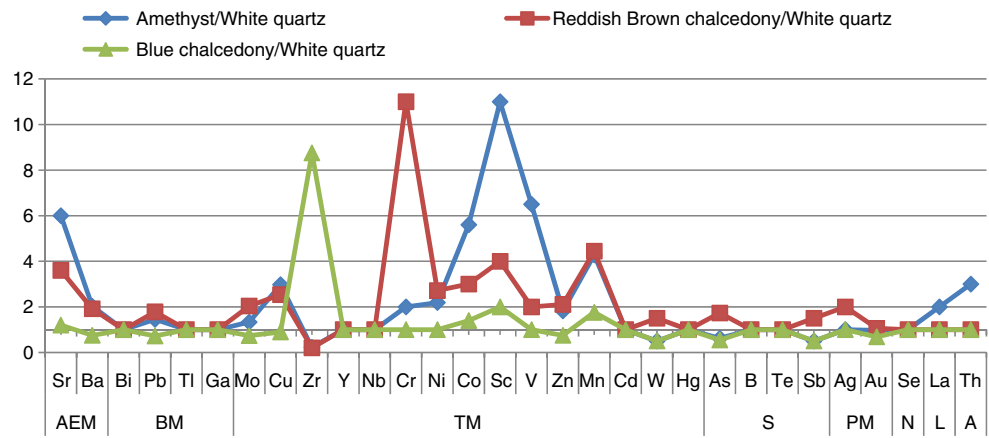


Fig. 11 Amounts of proportional ppm changes of amethyst, blue chalcedony, and reddish brown chalcedony in trace elements normalized to pure white quartz



salinity was between 3.06 and 4.96% NaCl. It was also reported that the temperatures of the solutions at the time when amethysts were formed were between 162 and 370 °C and the salinity was between 1.73 and 4.96% NaCl. Another finding was the transparent quartz-II formations at the last phase gave temperatures between 120 and 270 °C and salinity was between 0 and 6.88% NaCl. Chalcedony and amethyst formations in the Aydıncık-Yozgat region are thought to have been formed by the silicic waters with similar origins and development of chalcedony within the secondary calcite fillings

formed by calcium-rich waters in the fractures, cracks, and pores in the altered andesites in the area of investigation indicates that calcium-rich waters are abruptly replaced by the silica-rich waters in the ambient. It suggests that the phenomenon that could cause such a sudden change in the chemistry of the water forming the cracks and fracture fillings of the area of investigation might have been triggered by a volcanic or tectonic activity.

In the petrographic investigations made from thin sections of chalcedony and amethysts, quartz phenocrystals + quartz

Fig. 12 Ornaments made from the blue chalcedonies in the area of investigation



Fig. 13 Ornaments made from the amethysts in the area of investigation



Fig. 14 Ornaments made from reddish brown chalcedonies in the area of investigation



Fig. 15 Ornaments made from the white quartz in the area of investigation

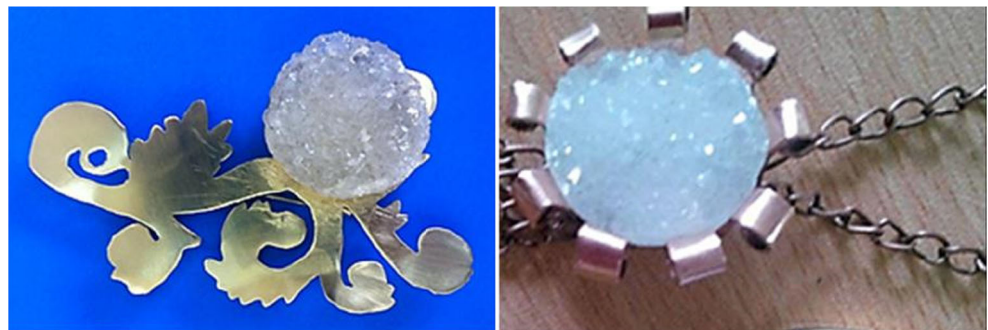




Fig. 16 Name badges made from ornaments made from the silicic gemstones with different colors and textures in the area of investigation

microcrystals + fibrous/acicular quartz minerals combination was found and calcite was found to accompany these minerals in some samples. In amethysts and chalcedonies, the opacity increases as grain size shrinks; as grain size grows, transparency increases.

XRD analysis made from white quartz, amethysts, and blue and reddish brown chalcedony specimens with different colors and textures revealed that all the specimens were composed solely of quartz mineral.

When the amethyst, blue chalcedonies, and reddish brown chalcedonies are compared to pure white quartz, the percent amount change in the main oxides is observed: a significant decrease in the amount of SiO_2 and enrichment in the amount of Al_2O_3 , Fe_2O_3 , MgO , and CaO . The enrichment of Fe_2O_3 in Turkey amethyst in major oxides is observed (Hatipoğlu et al. 2010b). In the study area, there is a significant enrichment in Fe_2O_3 and Al_2O_3 . Aluminum and iron elements are replaced by silicon atoms in the crystal structure. Hatipoğlu et al. (2013) in their studies, in blue chalcedony of Eskişehir-Turkey, the amount of Fe_2O_3 has determined 1.20% and the amount of Al_2O_3 has determined 0.01%. In the blue chalcedonies of our study area, the amount of Fe_2O_3 was found as 0.50% and the amount of Al_2O_3 was found as 0.08%. As a result, the blue chalcedonies in our region show a decrease in the amount of iron and a significant increase in the amount of aluminum, according to the blue chalcedonies in the Eskişehir region.

When the amethyst, blue chalcedony, and reddish brown chalcedony were compared to pure white quartz, trace element ppm changes were observed as follows: in amethyst and reddish brown chalcedony, enrichment of Sr, Ba, Pb, Cu, Cr, V, Zn, and Mn elements and decrease of Zr element; in blue chalcedony, decrease of Ba, Pb, Zn, and As and significant enrichment of Zr and Mn elements. According to different colored amethysts (dark purple, light purple, lilac, orchid, violet) in Balıkesir-Turkey (Hatipoğlu et al. 2011), trace element contents of amethyst in our region, in terms of Cr, Mn, As, Sr, Zr, Ba, La, Pb, and Th elements, were observed to be enriched (excluding La and Th elements in lilac) and these were

observed to be decrease in terms of Ni, Ga, Mo, Ag, Sb, W, and Au elements (except for Mo element in lilac).

The visible reserve of chalcedony and amethyst formations on the site together with many features such as rich color spectrum and continuity, their purity, stiffness, and resistance to acid and atmospheric conditions, durability, varnishing capacity, and reflection of light demonstrates that these stones have economic values that can be used as jewelry and gemstone.

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