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RESEARCH ARTICLE

COLOR CHANGE of TURQUOISE-COLORED COPPER SILICATE MINERALS EXAMINED by CHEMICAL, PHASE and MICROSTRUCTURE ANALYSIS

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ABSTRACT

In nature, copper silicate minerals generally have a turquoise color between the blue and green color spectrum. Turquoise color tones may vary depending on the stoichiometry and crystal structure in these minerals. In this study, the variation of color tones in copper silicate mineral with different turquoise colors was investigated. The causes of color change were investigated by chemical and mineralogical analyzes of copper silicate mineral in four different tones. Turquoise color becomes more vivid visually with increasing CuO and decreasing SiO_2 ratios. With changing stoichiometry, the crystal lattice parameters also change. The turquoise color of the minerals containing the highest (~16%) CuO and the lowest (~70%) SiO_2 has the best visual appearance compared to the others. For the same sample, the crystallite size was observed as 171 Å, which is the smallest crystallite size among the samples. In addition, SEM images and EDX analyzes of these samples were made and they were found to be consistent with mineralogical analyzes.

Keywords : *Copper Silicate, Turquoise, Color, Mineral.*

1. INTRODUCTION

Turquoise in copper silicate minerals can be considered as ornamental stones with their aesthetic structures. Turquoise color corresponds to different wavelengths between the blue and green spectrum [1]. The color tones of the turquoise copper silicate minerals found in nature also differ. Natural turquoise is a precious mineral known and used since early times with its unique color. The colors of the natural turquoise mineral can vary according to the elements it contains and their ratios. It is generally turquoise blue and bluish green in nature. Turquoise has a distinctive color. Its general formula is $CuAl_6(PO_4)_4(OH)_8.4(H_2O)$. It contains about 10% CuO and 35% P_2O_5, 38% Al_2O_3 [2].

Some minerals with similar color but with a totally different chemical composition are often mistaken for turquoises. This is the case of chrysocolla ($Cu_2.Alx(H_2xSi_2O_5)(OH)_4.nH_2O$ with $x < 1$), a hydrated copper silicate and, more recently, faustite ($(Zn,Cu)Al_6(PO_4)_4(OH)_8.4H_2O$) and blue prosopite ($(Cu, Al_2)(F,OH)_8$ [3-4].

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Chrysocolla, a turquoise- like mineral, is harder than turquoise. The general formula of Chrysocolla can be defined as $(Cu, Al)_2 H_2 Si_2O_5 (OH)_4 \bullet n(H_2O)$ [5].
In turquoise structure, iron ions show antiferromagnetic behavior at low temperatures and copper ions show paramagnetic behavior. In many turquoise structures, Fe^{2+} instead of Cu^{2+} and Fe^{3+} instead of Al^{3+} occur at varying rates. The characteristic spectrum and basic color (light blue) of turquoise is related to the presence of octahedral iron [6].

Crespo-Feo et al. determined the cathoduluminescence and thermoluminescence properties of turquoise. They stated that they gave weaker band emission between 260-650 nm and 750 nm in dense wide scattering in bulk samples. At the same time, they determined that there are apatite, monazite and xenotime minerals in the turquoise matrix [7].

Huifen et al. studied the magnetic properties, characteristic spectrum and color tones of turquoise. The basis of the studies is based on chemical data, magnetic susceptibility, absorption and Mössbauer spectrum. In their studies, it has been determined that the basic color of turquoise (light blue) is due to the presence of octahedral iron [8].

Three types of mechanisms work in the color change of minerals. These, molecular orbital transitions, crystal area and atomic point faults called color center are the main reasons for the formation of mineral colors. There are color changes during the production of turquoise colored ornamental stones produced synthetically, which spoils the aesthetic feature. For this purpose, turquoise colored copper silicate minerals found in Turkey were selected and separated according to different tonal colors and the factors causing color differences were investigated. In this study, natural turquoise was characterized as a preliminary research on the use of naturally occurring turquoise mineral as an alternative to synthetic pigment.

2. MATERIALS AND METHOD

The raw materials used in the study, copper silicate minerals, were obtained from Malatya Region in Turkey. Samples were separated by color and characterized. In order to determine the oxide content of the samples, chemical analyzes were carried out with PANalytical Brand AXIOS Model XRF device. Mineralogical content and phase analysis of the samples were made on the Rigaku X-ray Diffractometer model Rint 2000 device. Phase analysis was carried out at 30 kV and 15mA (Cu-Kα, λ=1,541 A^0, 2θ 5-70º, 2º/min.) conditions. In the analysis of XRD data for mineralogical and phase analysis, the JADE 6 software used with the device was scanned through PDF databases. For color measurements, measurements were made with the CIE system, which can quantitatively detect the differences in the material. Color analyzes of the samples were obtained by measuring L*, a*, b* values with a Konika Minolta 3600d spectrophotometer. The microstructural observations and qualitative chemical properties of samples were carried out using a field emission gun SEM (Zeiss Supra 50 VP) equipped with EDX system (Inca software), operated at 0-20 kV acceleration voltage under variable pressure without coating by using secondary and Back scattered electron imaging (SEI/BSEI) techniques.

3. RESULTS AND DISCUSSION

Photographs were taken to examine the color differences of the samples. The images of copper silicate minerals separated according to their colors are given in Figure 1. The samples are given in color

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order from dark turquoise to light turquoise in Figure 1a (sample name T1) and in Figure 1d (sample name T4), respectively.

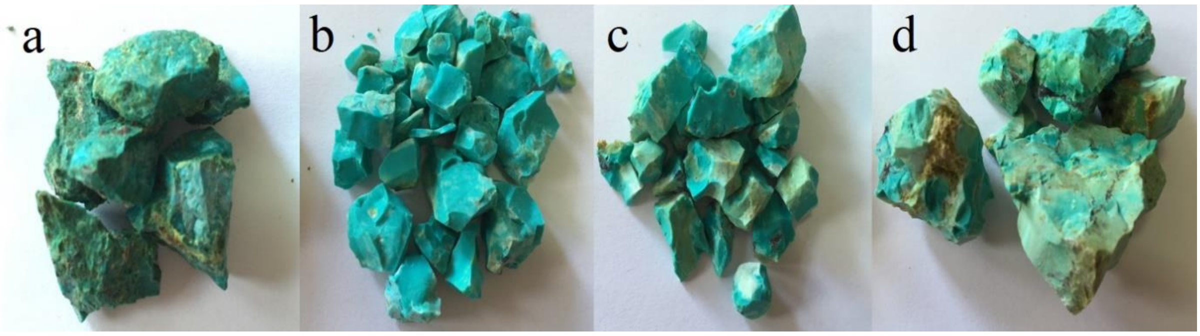

Figure 1. Copper silicate minerals listed according to their colors a) T1, b) T2, c) T3 and d) T4 sample.

Chemical analyzes of the samples were carried out in order to investigate the effect of chemical content on color change. The XRF analysis results of the samples are given according to their weight percent composition in Table1. SiO_2, CuO, MgO, CaO, Al_2O_3, Fe_2O_3 and PbO oxides were found in different proportions in all of the analyzed samples. From dark to light turquoise, the CuO ratios of the samples increased and SiO_2 decreased. Turquoise color changed according to copper oxide and silicon dioxide ratios. Turquoise colored samples vary between 6% and 16% CuO and 70% and 87% SiO_2 as the major oxide. The copper silicate mineral containing approximately 16% CuO and 70% SiO_2 has the most visually vivid turquoise color.

In the XRF analysis, it is seen that the Loss on ignition (LOI) in the samples have a very important in the content of the materials. This indicates that one or more of the minerals in the raw material contain water. The amount of LOI is lowest in T1, higher in T2, T3, and highest in T4 sample, respectively. This situation indicates that the mineral content of the T4 coded sample is the highest and the mineral content of the T1 sample is the lowest.

Table 1. Chemical analysis of turquoise colored minerals.

Sample No.	Oxide Ratios by Weight (%)							
	SiO_2	CuO	MgO	CaO	Al_2O_3	Fe_2O_3	PbO	LOI
T1	86.73	5.62	0.32	0.42	0.20	1.33	0.10	5.28
T2	80.06	11.40	0.28	0.22	0.23	0.60	0.04	7.17
T3	75.85	14.59	0.22	0.23	0.13	0.43	0.03	8.52
T4	69.49	15.60	0.34	0.57	0.14	0.50	0.10	14.01

L.O.I: Lost on ignition

X-Ray analysis was performed and the Rietveld method was used to determine the crystal parameters of copper silicate minerals. X-ray diffractograms of the samples are given in Figure 2. In X-Ray diffractograms of copper silicate minerals from dark color to light color, broadening peaks in the form of amorphization and humpback were observed. It has been determined that the XRD peaks of T4, which has the best turquoise color vividness, are in the amorphous phase formation, and its 2ϴ value

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is determined to widen the peaks between 20-27°. The peaks of T4 with turquoise color vividness are widened in the formation of amorphous phase and the peaks with two-theta value between 20-27°. The fact that the color of the same sample is more vivid is due to the higher ratio of dioptase and chrysocolla phases, which have amorphous-glassy structure. When the XRD diagram of T4 sample is examined, it is seen that the ratio of copper silicate phases is higher than the other 3 samples. It can be interpreted that the peak intensity of these minerals is high, and the amount of phase is high. In addition, the high amount of LOI in the XRF data also showed that the amount of copper silicate phase was high. These datas overlap with XRF, spectrophotometer and other analyses.

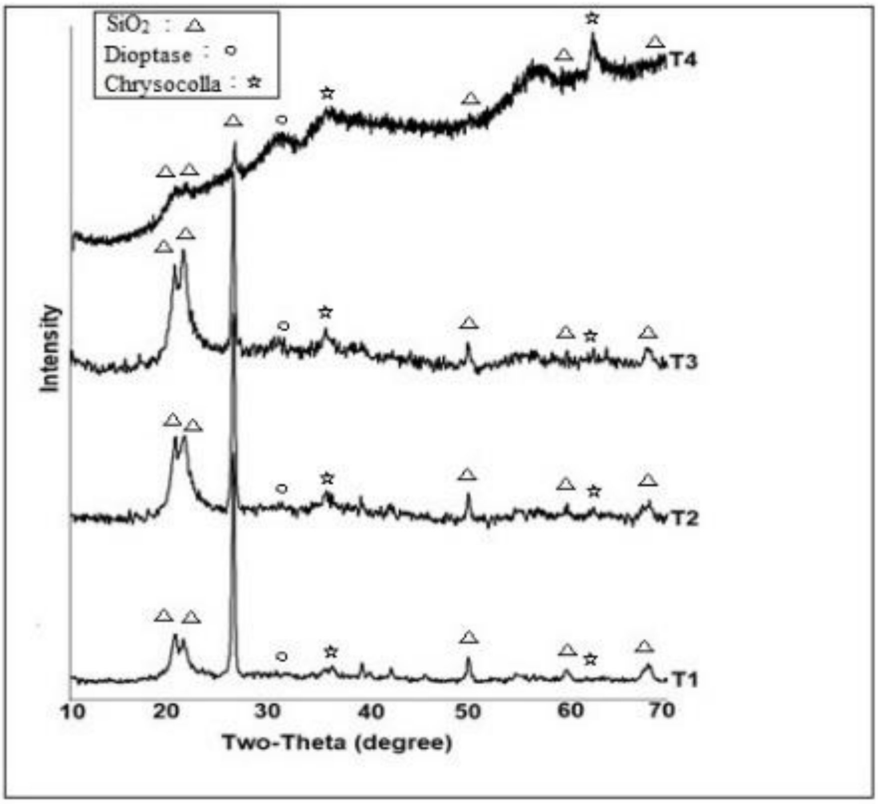

Figure 2. X-Ray diffractograms of minerals by color.

The lattice parameters calculated according to the Rietveld method are given in Table 2. The change rates of the smallest and largest axis values of the crystal parameters of the copper silicate minerals separated according to their colors were determined as 3.74% for the a-axis, 0.85% for the b-axis and 6.46% for the c-axis. The crystal parameters of T4, where the turquoise color is the most vivid, are at the highest values compared to the others. However, the crystallite sizes are the smallest with 170.76Å. The crystallite sizes decrease from about 746 Å to 171 Å from dark turquoise to light vivid turquoise. The color values of the samples were measured using a spectrophotometer and the obtained values are given in the same table (Table 2). In the system, which is defined as a three-dimensional coordinate axis, three values consisting of L* (brightness axis), a* (red-green) and b* (yellow-blue axis) were measured. The purpose of this analysis is to show by numerical measurement of color values that minerals have effective mechanisms such as absorbing certain energies of light or exposing them to direct emission, based on Kurt Nassau's work in 1978. In this way, it guides the determination of the change in the color values of atoms excited to high energy levels by the incoming light energy [9,10]. The crystal parameters of the T4, which have more vivid colors compared to the others, are larger than the others, and their color coordinates are at the highest values. The color differences of the samples, as well as shown in Figure 1, were also confirmed by spectrophotometer measurement.

Table 2. Lattice parameters and color values according to colors.

Sample No.	Crystal Parameters				Color Coordinates		
	a-axis	b-axis	c-axis	Crystallite Size	L*	a*	b*
T1	21.887	21.193	16.036	745.895	-76.19	-19.46	1.03
T2	21.936	21.144	15.962	415.827	-69.48	-16.76	5.40
T3	21.897	21.131	16.047	388.289	-67.65	-15.45	3.22
T4	22.705	21.310	16.993	170.76	-54.88	-14.79	6.77

In the chemical analyzes of copper silicate minerals in four different turquoise tones, CuO increases while SiO_2 decreases. Microstructure examinations of the same samples were made and their images are given in Figure 3. In the analysis, it was determined that the SiO_2 ratio was higher in morphological crystals with large grains (Figure 3a and b). It was determined that small crystallite particles were collected on the large particles and that the small particles were dioptase and chrysocolla copper-silicate based particles. Average values of EDX analyzes taken from selected areas 1, 2, 3 and 4 areas in Figure 3 are given in Table 3. Likewise, SiO_2 decreased and CuO ratios increased in the EDX analyzes of the samples in which the turquoise color changed from dark to light. Crystal particles are not in micrometer size, but rather in nanometric size.

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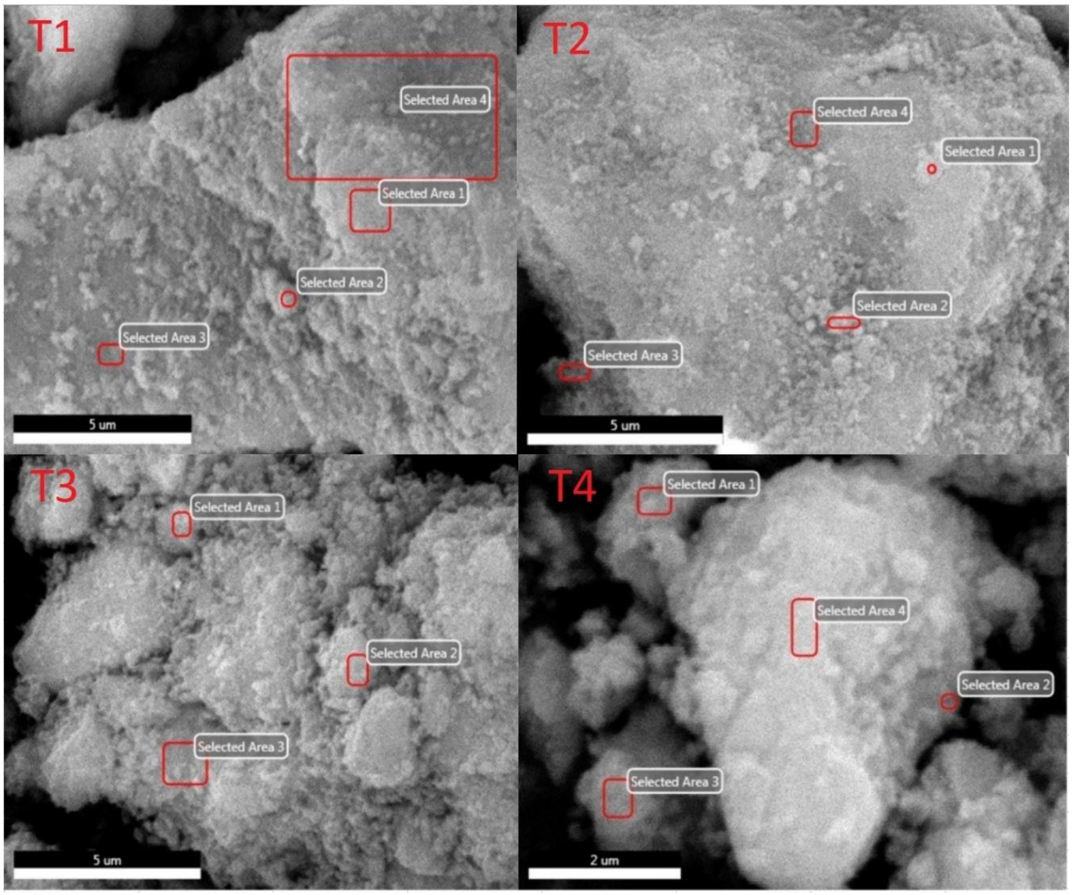

Figure 3. Microstructure images of samples in different colors

EDX analyzes from the surfaces of copper silicate minerals showed that SiO_2 was higher in dark colored minerals and CuO was higher in light colored minerals (Table 3). It was determined that the turquoise color would be more vivid with the increase in the CuO/SiO_2 ratio. Accordingly, the CuO/SiO_2 ratio of copper silicate minerals in the range of 1.4 to 2.7 is important in the visuality of the turquoise color. The chemical content of the samples obtained as a result of XRF analysis coincides with the data obtained as a result of EDX analysis.

Table 3. EDX analyzes of copper silicate minerals in four different colors.

Oxides	T1 (%wt)	T2 (%wt)	T3 (%wt)	T4 (%wt)
SiO_2	92.64	80.23	70.37	53.65
Fe_2O_3	2.31	-	-	-
CuO	6.04	19.78	29.63	46.35

4. CONCLUSION

The results obtained in the study can be listed as follows:

- ✓ Samples were separated by color and characterized.
- ✓ Turquoise colored copper silicate minerals are more vivid in color with increasing CuO and decreasing SiO_2 ratios. In addition, it was determined that the change of turquoise color from light to dark tones in turquoise pigments depends on CuO and SiO_2 changes.
- ✓ The crystal lattice parameters of the copper silicate mineral changed with the change of oxide ratios. With increasing CuO ratio, the lattice parameters were the highest at a-axis 22.705 Å, b-axis 21.310 Å and c-axis 16.993 Å.
- ✓ The crystallite sizes decreased with increasing CuO ratio and decreasing SiO_2 ratio. Turquoise color appearance has a more vivid appearance with decreasing crystallite size.
- ✓ The smallest crystallite size was determined as 171 Å in the most vivid turquoise colored copper silicate mineral. As the crystallite size decreased, the turquoise color appearance was visually better.
- ✓ The starting raw material used is not the copper silicate sample turquoise mineral. The samples contain predominantly SiO_2 and less dioptase and chrysocalla minerals. Because turquoise is a semi-precious stone, it is costly. Since copper silicate-based specimens are less costly to extract and process, they can be used to make ornamental stones or tiles.

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