TURQUOISE FROM ZHUSHAN COUNTY, HUBEI PROVINCE, CHINA

Quanli Chen, Zuowei Yin, Lijian Qi, and Yan Xiong

A relatively new source of gem-quality turquoise is hosted within slates in Zhushan County of China's Hubei Province. Rough and polished samples were studied using standard gemological methods, as well as FTIR and UV-Vis-NIR spectroscopy. The turquoise formed nodular, massive, and veinlet assemblages. Brown and black veinlets/patches and irregular white blebs were common, and microscopic observation also revealed microcrystalline and spherulitic structures. In general, the nodular specimens were of the highest quality. The deposits show considerable potential as a commercial source of gem-quality turquoise.

China has been a significant source of turquoise for decades. One area of Zhushan County in Hubei Province has produced some attractive material (e.g., figure 1), but it has been overshadowed by more productive turquoise deposits in nearby Yun County (Tu, 2000). Chinese turquoise is also known from the city of Ma'anshan in Anhui Province, Baihe County in Shaanxi Province, and the Xichuan area of Henan Province.

The turquoise from Yun County is regarded as superior in quality (Ma, 1989; Qi et al., 1998; Tu, 2000). The output from Yun County between 1954 and 1999 totaled more than 800 tonnes, according to data provided by local officials, but its resources are depleting. The deposits in Zhushan County (figure 2) were found in the late 1980s, yet much is still unknown about their distribution and complex geologic formation. While the material from Zhushan County is often of high quality, with a dense texture and an attractive uniform coloration, mining activity has only recently begun.

LOCATION AND GEOLOGIC BACKGROUND

The Zhushan County turquoise deposits are located in a mountainous region of central China (again, see figure 2). More than 100 mine tunnels have been worked (e.g., figure 3), the deepest reaching ~300 m. The turquoise occurs in the Cambrian-age Shuigoukou Formation, within thick- and thin-bedded siliceous and carbonaceous-siliceous slates. The mineralized zones generally extend northeast-southwest and follow the regional tectonic structure. The turquoise is found mostly as lenses along faults and as fillings within fractures (figure 4). The highest quantity and quality of turquoise is typically found where faulting created

Figure 1. This carving, called "Eight Immortals," was made from a large piece of Zhushan County turquoise. It measures 23 cm high and 27 cm wide. Photo by Quanli Chen.

See end of article for About the Authors and Acknowledgments.
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compressive intercalated lenses. The turquoise is often associated with carbonaceous material, limonite, secondary quartz, kaolinite, allophane, and other clay minerals (Tu, 1996). The largest documented block of turquoise weighed 100 kg, according to data from the local government. Turquoise production from Zhushan County as a whole ranges from 50 to 129 tonnes annually.

Figure 3. Zhushan County turquoise is produced from underground workings that follow the turquoise mineralization to depths of ~300 m. Photo by Quanli Chen.

TREATMENTS

Turquoise from Zhushan County possessing a compact structure usually does not require treatment. Specimens with low hardness and a less compact structure are impregnated with an organic polymer such as polyacrylic acid ester or plastic, using the following process:

(1) Drying the turquoise and placing it under vacuum
(2) Impregnation with an organic polymer under high pressure
(3) Heating to solidify the polymer

This is the most commonly used turquoise treatment process in China, intended to improve the density, hardness, and toughness of the material. If a colored polymer is used, the turquoise's color will also be improved. The treatment can be identified by the presence of ν (CH_2) absorption features in the 2930–2857 cm^{-1} region of the infrared absorption spectrum (Chen et al., 2006).

Figure 2. This map shows the location of turquoise deposits in Zhushan County, Hubei Province.

MATERIALS AND METHODS

Eight rough and four polished turquoise samples from Zhushan County were studied for this report (figure 5). They were all untreated, and the rough material was obtained from the mines. Gemological properties were determined with standard equipment. Eight of the samples were tested for RI and Mohs hardness. Specific gravity measurements were performed on 10 samples; fine-textured specimens were measured hydrostatically, while less-compact pieces were cut into cubes and their weight was divided by their volume. Petrographic analysis was per-

In Brief

- Known since the late 1980s, turquoise deposits in Zhushan County in central China's Hubei Province are becoming a significant source of attractive material.
- The turquoise forms lenses and fracture fillings within Cambrian-age slates.
- Although most Zhushan turquoise does not require treatment, lower-quality material usually undergoes polymer impregnation.
- Most characteristics of Zhushan turquoise, including the presence of brownish black veinlets/patches and irregular white blebs, are similar to those noted in samples from elsewhere in Hubei Province.

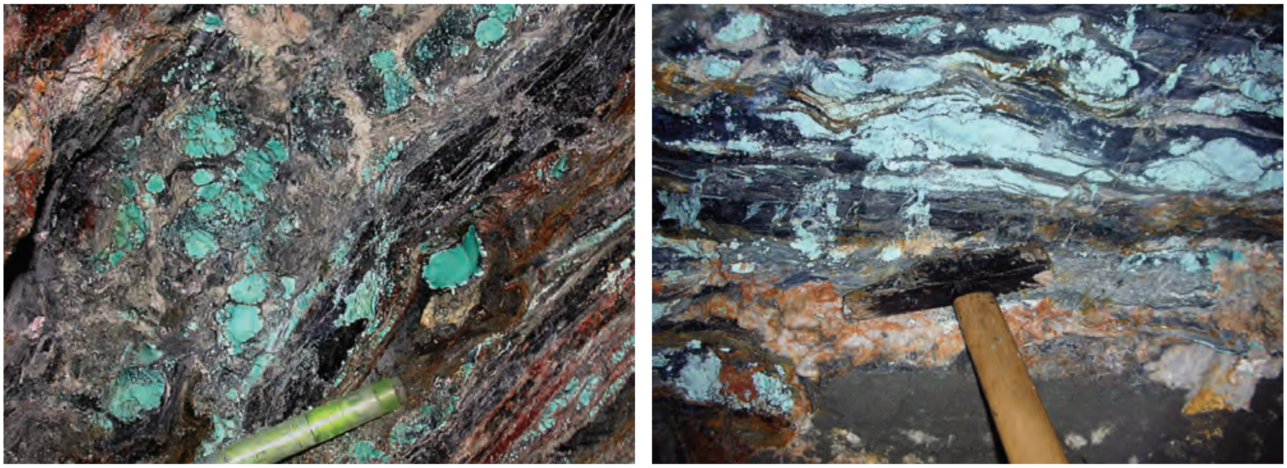

Figure 4. The turquoise occurs as lenses and fracture fillings in a compressed fractured zone between beds of siliceous and carbonaceous-siliceous slates. Photos by Quanli Chen.

formed with a polarizing microscope to study the mineralogical and textural features of the turquoise (using thin sections cut from six of the rough samples) and the surrounding rocks.

Five rough samples were prepared for bulk chemical analysis by grinding them into powder with an agate mortar and sieving to 200 mesh. Impurities were avoided as much as possible to ensure the accuracy of the analyses. In accordance with the requirements of GB/T14506-2010, China's national standard for rock chemical analysis, the contents of Na, K, Ca, Mg, Cu, and Zn were measured with a Hitachi 180-70 atomic absorption spectrometer; Ti and Fe^{3+} with a Hitachi UV-754 UV-Vis spectrophotometer; Si and H_2O through the hydrochloric acid content of the secondary dewatering measured weight method; Fe^{2+} by redox titration; Al through complex titration with ethylenediaminetetraacetic acid; and P through phosphomolybdate blue spectrophotometry.

Infrared spectra were recorded on four samples using a Nicolet Magna 550 FTIR spectrometer. Spectra were obtained in the 4000–400 cm^{-1} range by combining 32 scans with a resolution of 4 cm^{-1} and a mirror velocity of 0.63 cm/sec. All spectra were recorded from 1–2 mg of powdered turquoise mixed with 200 mg of pure KBr. The powders were derived from four structural types of samples: nodular, oolitic, veinlet, and grape-like.

UV-Vis-NIR absorption spectra were measured on polished plates of the same four rough samples chosen for IR spectroscopy. We used a Shimadzu UV-1601 spectrophotometer in the 400–900 nm range, with a step size of 0.5 nm and a scan rate of 2.64 nm/sec.

RESULTS AND DISCUSSION

Gemological Features. The Zhushan County turquoise occurs mainly as veinlets, blocks, and nodular aggregates (figure 6). It is generally compact, massive, and shows a waxy luster. Its color is predominantly a medium bluish green. Light bluish green, light green, and yellowish green are also fairly common, while "azure" blue is rare. Oolitic and grape-like structures are sometimes seen, while turquoise with a nodular texture is of the highest quality and ranges up to 50–60 cm in maximum dimension; its surface is characterized by bulbous irregularities (see figure 6, right). Similar turquoise comes from Yun County, typically with a tubular shape and a blue-green color.

Figure 5. These rough (left, 3.74–11.48 g) and polished (right, 3.35–6.86 ct) samples of turquoise were examined for this report. Photos by Quanli Chen.

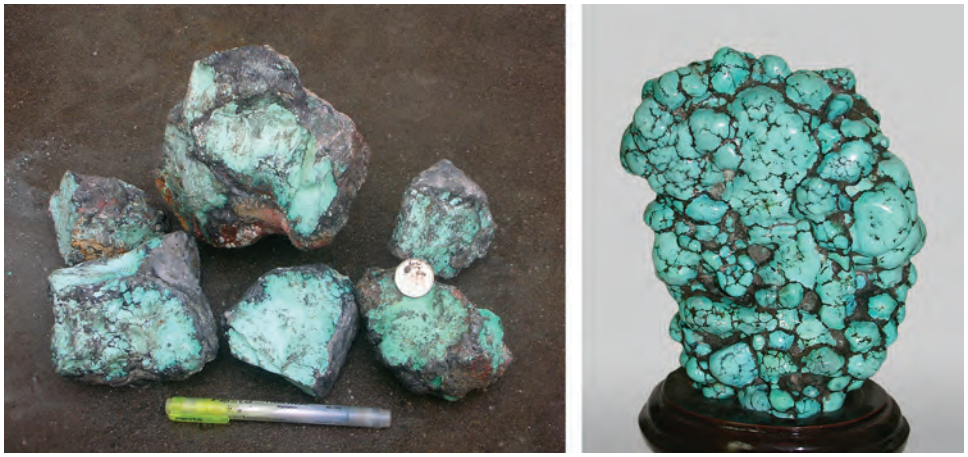

Figure 6. Blocky turquoise is commonly produced from the Zhushan County deposits (left). Nodular specimens are usually displayed as ornamental stones (right, 30 × 22 cm). Photos by Quanli Chen.

Our turquoise samples showed the following properties: RI—1.61–1.62; Mohs hardness—5–5½; and SG—2.57–2.72. Thin-section examination revealed microcrystalline plate-like and spherulitic structures (figure 7). The turquoise matrix was composed mainly of carbonaceous material, limonite, and a clay mineral. Secondary quartz is locally present in the matrix as elongate bladed aggregates. The slate host rock shows a platy, fine-grained crystalloblastic texture.

Brownish black veinlets/patches and irregular white blebs are typical features of turquoise from Zhushan County (figure 8). The brownish black areas were identified as carbonaceous material and iron oxides or hydroxides, while the white impurities were formed by quartz and kaolinite (Qi et al., 1998; Zhang, 2006). These minerals are also frequently found in specimens from Yun County (Li et al., 1984; Qi et al., 1998; Luan et al., 2004). Other similarities in the turquoise from these two areas include their textures seen in thin section and their formation within siliceous-carbonaceous slates (Jiang et al., 1983; Qi et al., 1998).

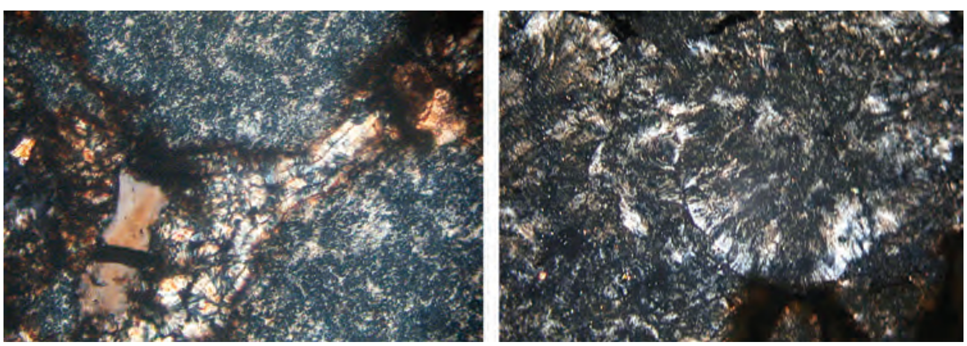

Figure 7. Viewed with crossed polarizers, these turquoise thin sections show microcrystalline plate-like textures (left photo, top and lower right areas) and spherulitic structures (right). Photomicrographs by Lijian Qi; magnified 100×.

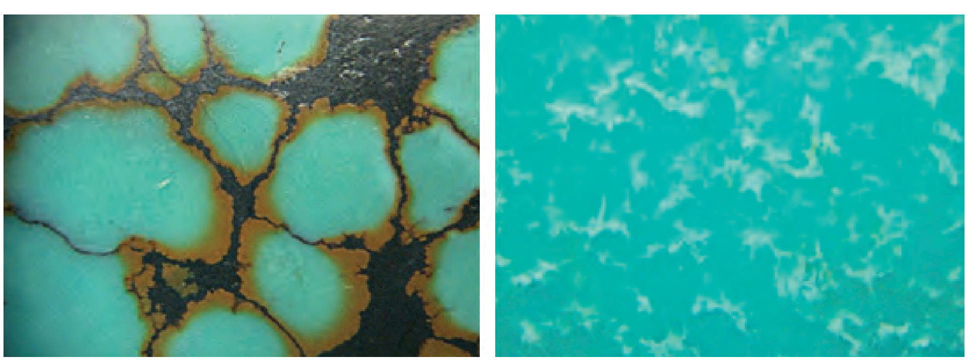

Figure 8. The turquoise usually contains brownish black veinlets/patches (carbonaceous material and iron oxides or hydroxides) and white blebs (quartz and kaolinite). Photos by Lijian Qi; magnified 100×.

TABLE 1. Chemical composition of turquoise samples from Zhushan and Yun Counties.[a]

	Zhushan County[b]					Yun County (Qi et al.,1998)		Yun County (Luan et al., 2004)	
Oxide (wt.%)	Pale blue-green (Q-2)	Blue-green (Q-3)	Light blue-green (Q-6)	Blue (Q-10)	Light blue (Q-21)	Blue	Blue-green	Blue	Blue-green
SiO_2	0.02	0.06	0.50	0.20	0.16	nr	nr	0.90	0.05
Al_2O_3	33.46	34.90	33.50	36.30	36.15	35.92	35.57	38.29	32.50
Fe_2O_3	4.21	5.57	6.58	1.43	1.13	1.21	2.70	0.31	8.97
FeO	0.32	0.18	0.06	0.09	0.08	nr	0.03	nr	nr
MgO	0.02	0.01	0.01	0.01	0.01	nr	nr	nr	nr
CaO	0.02	0.03	0.01	0.04	0.02	0.04	nr	nr	nr
Na_2O	0.01	0.02	0.03	0.01	0.01	nr	nr	nr	nr
K_2O	0.03	0.03	0.02	0.02	0.01	nr	nr	nr	nr
TiO_2	bdl	0.06	0.02	bdl	bdl	nr	nr	nr	nr
P_2O_5	33.16	31.12	31.69	33.80	33.52	34.64	34.15	34.22	34.81
CuO	5.87	3.97	3.75	7.63	6.17	8.34	7.17	8.55	7.93
ZnO	0.09	0.08	0.04	0.12	0.92	nr	nr	0.44	0.14
H_2O	21.96	22.24	22.82	20.09	23.38	19.75	20.32	nr	nr
Total	99.17	98.24	99.03	99.74	101.56	99.90	99.94	82.80	84.40

[a] *Abbreviations: bdl = below detection limit, nr = not reported.*
[b] *Sample numbers are shown in parentheses.*

Chemical Composition. Turquoise, with a chemical composition of $CuAl_6(PO_4)_4(OH)_8{\cdot}4H_2O$, is a hydrous copper aluminum phosphate. Our samples contained 1.21–6.64 wt.% total iron oxide (table 1), showing they belong to the turquoise-chalcosiderite family (Frost et al., 2006). The bluer samples contained higher Cu and lower Fe concentrations. Although they displayed various colors, the main chemical constituents Al_2O_3, P_2O_5, and H_2O were relatively stable and comparable to samples from Yun County (again, see table 1).

IR Spectroscopy. IR spectra of turquoise show distinct sets of bands related to phosphate, water, and hydroxyl units (figure 9). Our samples had absorption bands attributed to the stretching vibrations of OH and H_2O at ~3510, 3463, 3290, and 3086 cm^{-1}, and a 1638 cm^{-1} band assigned to the bending vibration of H_2O (Chen et al., 2007; Frost et al., 2006; Reddy et al., 2006). Four bands assigned to the ν_3 asymmetric stretching vibrations of phosphate units were recorded at approximately 1157, 1107, 1058, and 1011 cm^{-1}. In addition, we detected two weak bands at ~835 and 786 cm^{-1} caused by the bending vibration of OH units. Other features from approximately 647 to 482 cm^{-1} were due to the phosphate ν_4-bending modes. No evidence of treatment was found in the IR spectra of our samples.

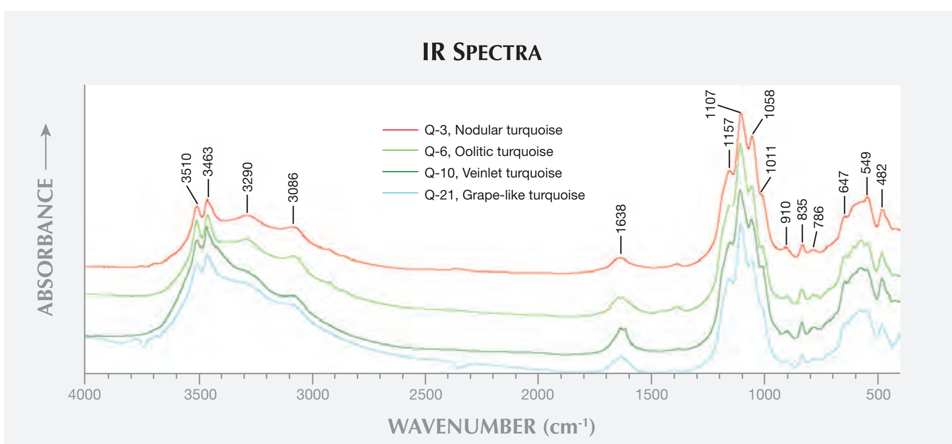

Figure 9. All four of the Zhushan turquoise samples tested showed very similar IR spectra, with typical bands related to phosphate, water, and hydroxyl units.

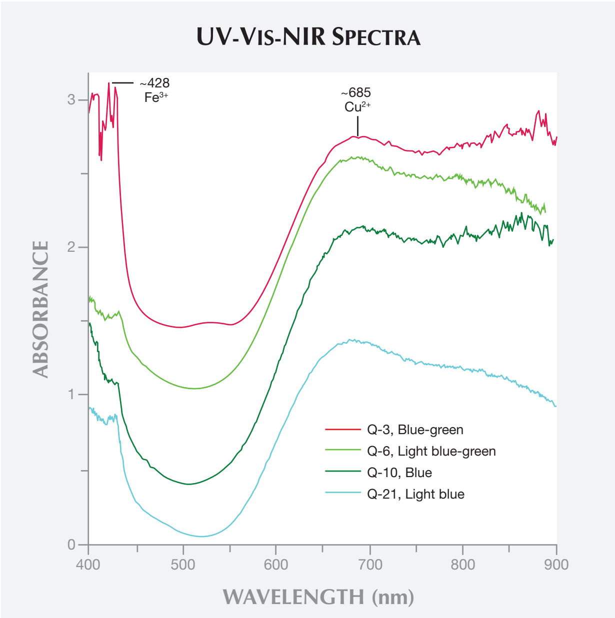

Figure 10. Four different-colored turquoise samples showed absorption bands caused by Fe^{3+} d-d electronic transition (~428 nm) and Cu^{2+} d-d electronic transition (~683–688 nm).

These infrared features are very similar to those of turquoise from Yun County (Farmer, 1982; Zhang et al., 1982; Qi et al., 1998).

UV-Vis-NIR Spectroscopy. Figure 10 shows the UV-Vis-NIR absorption spectra of four different-colored samples. Turquoise coloration depends on Fe^{3+} and Cu^{2+} transition metal content (Qi et al., 1998), which corresponds to two diagnostic absorption bands: a strong and narrow band centered at ~428 nm caused by Fe^{3+} d-d electronic transition, and a broad absorption centered at ~685 nm due to Cu^{2+} d-d electronic transition. The UV-Vis-NIR absorption spectra of all four samples were similar.

CONCLUSIONS

Turquoise in China's Zhushan County (e.g., figure 11) occurs in a compressed fractured zone among beds of siliceous and carbonaceous-siliceous slates. The turquoise is characterized by a variety of forms and colors, though it is typically medium bluish green. Microscopic examination of thin sections shows microcrystalline plate-like and spherulitic structures. Brownish black veinlets/patches and irregular white blebs are common. The infrared absorption spectra show typical phosphate, water, and hydroxyl vibrations for turquoise. UV-Vis-NIR absorption spectra have strong, sharp bands caused by Fe^{3+} and wide bands caused by Cu^{2+}. Most of the gemological and spectral characteristics of turquoise from Zhushan County are similar to those found in samples from elsewhere in China's Hubei Province. There are strong indications (e.g., Guo, 2004) that the Zhushan County deposits have significant potential for development.

Figure 11. This jewelry features turquoise from China's Zhushan County. The beads measure ~4 mm in diameter. Photo by Yan Xiong.

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