The Identification of Turquoise by Infrared Spectroscopy and Energy Dispersive X-ray Fluorescence Spectrometry

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Abstract

Turquoise has been subjected to various methods of treatment in order to improve its marketability as a gem material. Treatments include efforts to enhance color or reduce porosity. In addition, a number of turquoise imitations are found on the gemstone market. The separation of natural, untreated turquoise from its treated counterpart, and the distinct identification of imitation or synthetic turquoise is difficult using the routine gemological methods generally used. However, a combination of infrared spectroscopy and energy dispersive X-ray fluorescence spectrometry methods is suggested for the identification of natural, treated, and synthetic turquoise as well as imitation turquoise.

Introduction

Many processes are used to improve the appearance and durability of turquoise. For hundreds of years, the chalky (low quality) turquoise with low specific gravity and high porosity has been treated with paraffin, oils, and various other substances to deepen the color and fill the pores to make this inferior material appear less chalky and more desirable. Primarily turquoise too porous for cutting was plastic-impregnated (with paraffin, oils, and various other substances) to improve the hardness of the specimen.

Currently, good-quality turquoise is also treated by plastic impregnation (with paraffin, oils, and various other substances) in order to improve the durability of the material. There is a relatively new, proprietary turquoise treatment, commonly known in the trade as "enhanced turquoise", which cannot be detected by any of classical methods. In addition, a number of turquoise imitations and synthetic turquoise are found on the gemstone market.

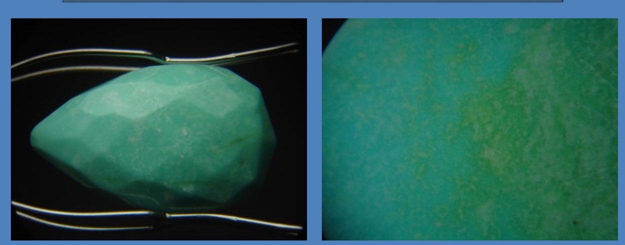
Physical and optical properties of turquoise

1. Refractive index : from 1.60 to 1.62 (spot method)
2. Color : Light sky blue, greenish blue, bluish green and green color
3. Transparency : Opaque
4. Hardness : 5 ~ 6
5. Specific gravity : 2.40 ~ 2.90
6. Crystal system : Triclinic
7. Composition : $CuAl_6(PO_4)_4(OH)_8 \cdot 5H_2O$ (Hydrated copper aluminum phosphate)
8. Fluorescence : Weak greenish yellow
   (Long- and short-wave ultraviolet radiation)
   Long-wave ultraviolet radiation : Weak to moderate whitish blue
   Short-wave ultraviolet radiation : Inert
9. Optical absorption spectrum : Band at about 432 nm and 460 nm

Gemological properties of natural and treated turquoise, of Gilson synthetic turquoise, and of various imitation turquoise

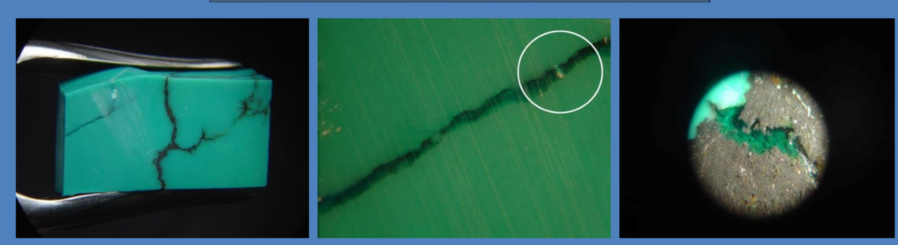
	Natural turquoise	Treated turquoise	Gilson synthetic turquoise	Imitation turquoise (gibbsite)	Various imitation turquoise
Refractive indices	1.60 or 1.61 (spot)	1.60 or 1.61 (spot)	1.60 or 1.61 (spot)	1.57 (spot)	from 1.53 to 1.62
Specific gravity	2.40 ~ 2.90	2.30 ~ 2.50	2.40 ~ 2.90	2.30 ~ 2.40	2.18 ~ 2.63
Hardness (Mohs)	5 ~ 5.5	same or lower than natural turquoise	5 ~ 5.5	2.5 ~ 3	lower than natural turquoise

Natural Turquoise



Gilson Synthetic Turquoise

Treated Turquoise

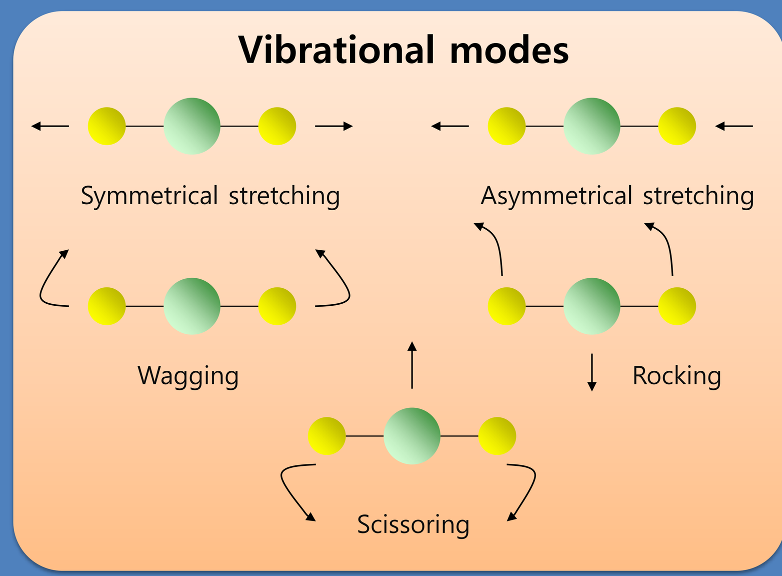


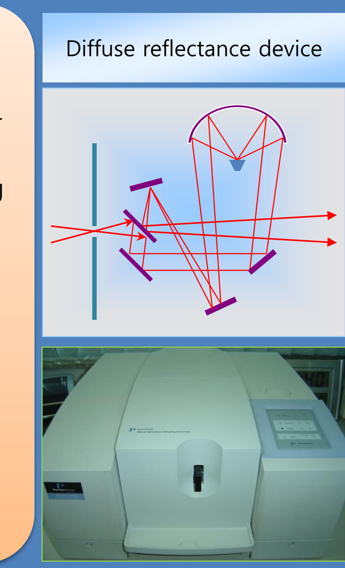
Identification by advanced testing

1. FTIR : Principle of the method

The fundamental vibration energies in the structures of many gemstones are located in the mid infrared region, typically between 1500 ~ 400 cm^{-1} and use of reflectance techniques can detect these.

The infrared absorption caused by structural vibrations is determined by bond lengths and bond angles between the atoms and has been described as the 'fingerprint zone'.



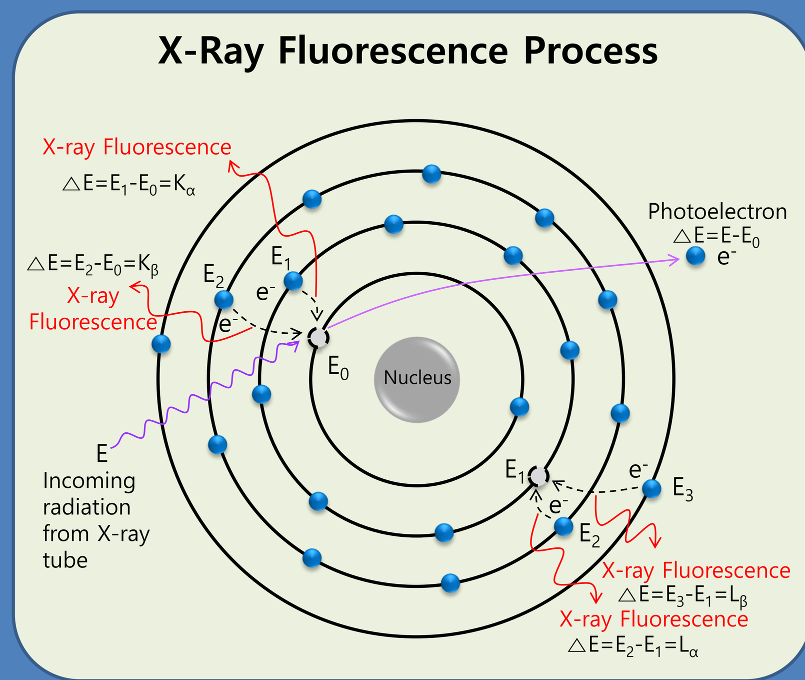


2. EDXRF : Principle of the method

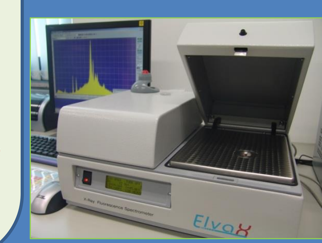
An electron in the K shell is ejected from the atom by external primary excitation x-ray, creating a vacancy.

An electron from the L or M shell "jumps in" to fill the vacancy. In the process, it emits a characteristic x-ray unique to this element and in turn, produces a vacancy in the L or M shell.

When a vacancy is created in the L shell by either the primary excitation x-ray or by the previous event, an electron from the M or N shell "jumps in" to occupy the vacancy. In this process, it emits a characteristic x-ray unique to this element and in turn, produces a vacancy in the M or N shell.



The emitted x-rays produced from this process are called "X-ray Fluorescence" or XRF.



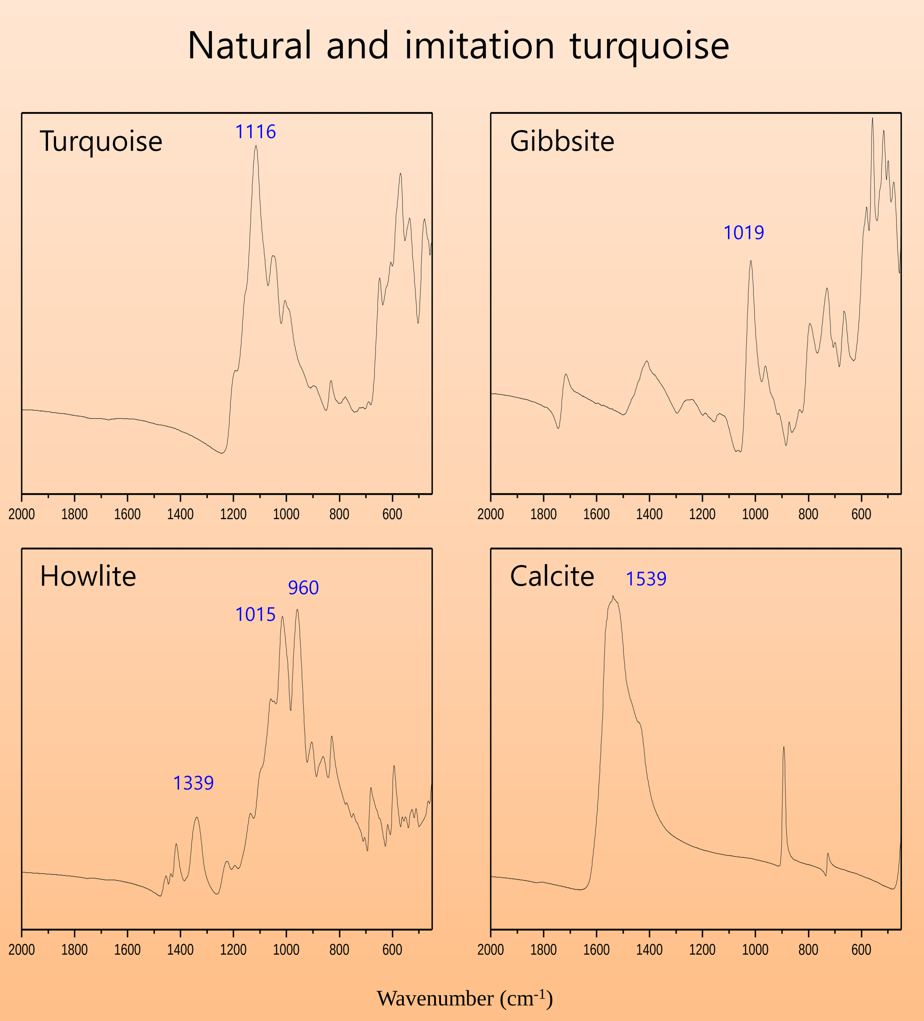
Results

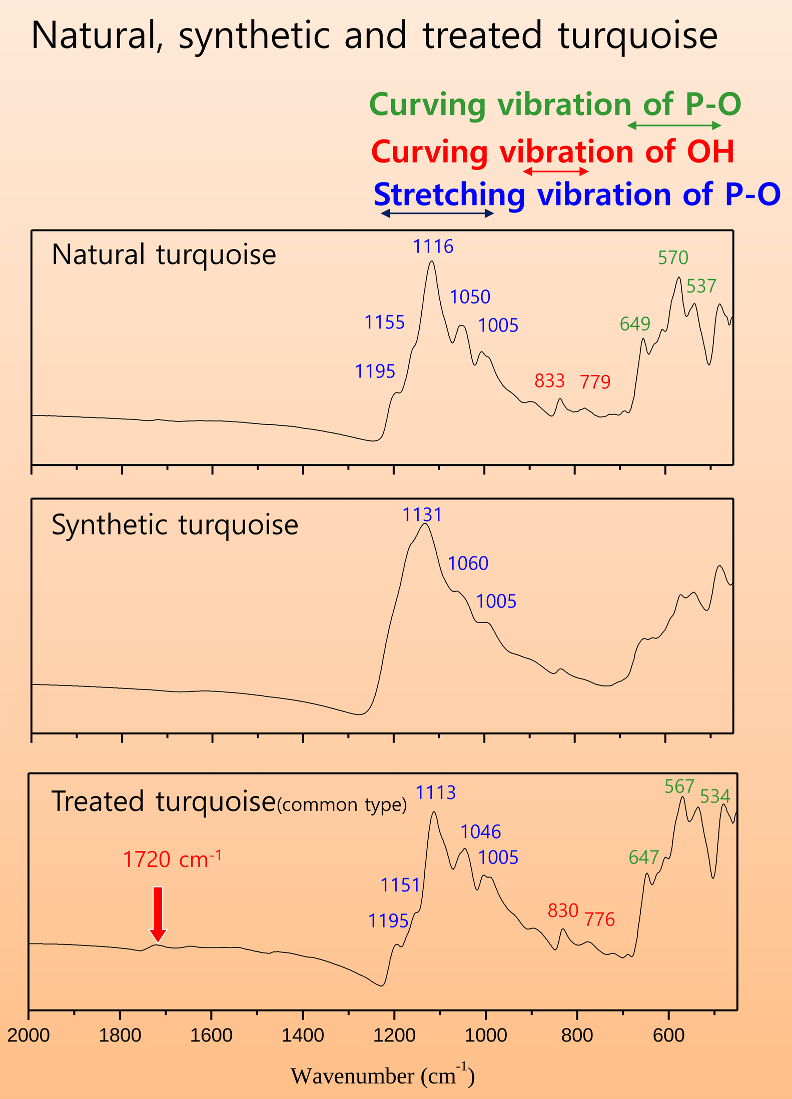
Natural turquoise can be distinguished easily from its common substitutes, which are gibbsite (a clay-like aluminum hydroxide), calcite, dolomite and howlite, through features observed in the mid infrared region. Gilson synthetic turquoise exhibits a significantly smoother pattern when compared with natural turquoise. In the infrared spectrum of the plastic-impregnated turquoise investigated in this study, a strong infrared absorption band at 1720cm^{-1} was observed, in addition to the characteristic absorption bands of turquoise in the area of the vibrations of the hydroxyl and phosphate groups. However, the absorption band at 1720 cm^{-1} is not observed in natural turquoise. EDXRF results show that the natural, treated and synthetic turquoise are basically $CuAl_6(PO_4)_4(OH)_8 \cdot 5H_2O$, but the major constituents of imitation turquoise could still be detected: Al, Mg and Ca. Although the color of natural and treated turquoise is variable, its main chemical constituents, aluminum (Al), phosphorus (P), and copper (Cu), are relatively stable.

Iron (Fe), a common impurity in turquoise, is detected in all samples. The height of the Fe peak correlates to the green component of the color, that is, the green samples show the most intense Fe peaks. Sulfur (S) can also occasionally be detected. Its signal is stronger in samples containing pyrite (FeS) inclusions. Traces of the common transition elements titanium (Ti), chromium (Cr), and vanadium are also present in some natural and treated turquoise. A small potassium (K) peak is sometimes present in the natural material, but it is always smaller than the calcium (Ca) peak. Conversely, the treated turquoise usually shows much higher K peaks. EDXRF, for the identification of a turquoise, is not helpful to distinguish natural turquoise from synthetic turquoise, yet is nevertheless reliable for identification of natural turquoise from some color treated or imitation turquoise.

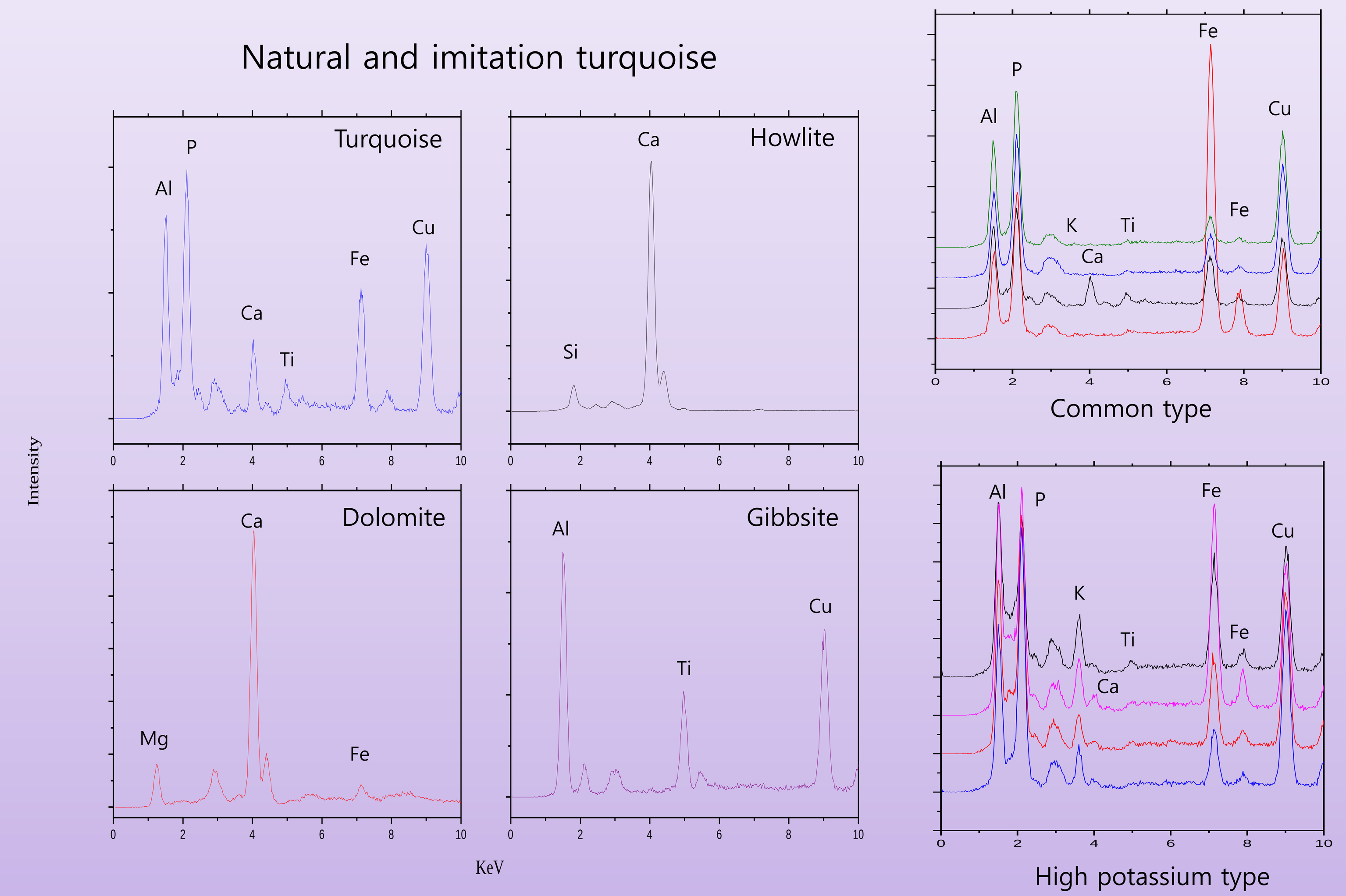
In conclusion, judicious use of FTIR and EDXRF techniques can effectively distinguish various forms of turquoise, turquoise look-alikes and man-made imitation turquoise.

Infrared spectra





EDXRF spectra



Conclusion

1. **Gilson turquoise, which is a synthetic, exhibits a significantly smoother pattern when compared with natural turquoise, because of a different state of aggregation.**
2. **Because the natural turquoise and imitation turquoise are so different chemically, their patterns are very different.**
3. **The treated turquoise of two type can be identified by relatively high potassium levels and the peak at 1720cm^{-1}.**
4. **In conclusion, judicious use of FTIR and EDXRF techniques can effectively distinguish various forms of turquoise look-alikes and man-made imitation turquoise.**