



Technical Note

Fake turquoises investigated by Raman microscopy

Nathália D'Elboux Bernardino^a, Celly M.S. Izumi^b, Dalva L.A. de Faria^{a,*}^a Depto. de Química Fundamental – Instituto de Química da USP, Av. Prof. Lineu Prestes, 748 – Butantã, 05508-000 São Paulo, SP, Brazil^b Departamento de Química – Universidade Federal de Juiz de Fora, Rua José Lourenço Kelmer, s/n – Martelos, 36036-900 Juiz de Fora, MG, Brazil

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ABSTRACT

Turquoise is frequently adulterated by unscrupulous dealers and, not rarely, simulants are commercialized as true stones. On the other hand, turquoise is a cryptocrystalline mineral and its use in adornments commonly demands some kind of treatment to facilitate its manipulation, such as impregnation using oil or fats, consolidation with resin and stabilization or reconstitution made with resins. In this work, Raman microscopy was employed in the investigation of turquoise adornments aiming to differentiate processed turquoise from fakes or simulants. Only one out of the five adornment objects analyzed was truly stabilized turquoise (powdered turquoise aggregated with a resin). Another one was constituted of turquoise, calcium carbonate, phthalocyanine blue and resin; the other objects were dyed minerals.

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1. Introduction

Gemstones have always occupied an important position in human history [1], mostly due to their attractive colors or other optical properties such as high reflectivity [2]. This fascination was so intense that magical and healing properties were assigned to some gems [3] which, when rare, were used as a representation of power and wealth. As jewelry, such stones can reach extremely high values and for this reason are frequently targeted by unscrupulous persons devoted to obtain large profits by simulating precious stones from several materials or adulterating the stone properties by means of physical (heat and gamma irradiation, mostly [4]) or chemical (dyes, enhancers, whiteners, oils and resins for example [5,6]) treatments.

Turquoise ($\text{CuAl}_6(\text{PO}_4)_4(\text{OH})_8 \cdot 4\text{H}_2\text{O}$) presents a characteristic blue or greenish blue color and are found in objects produced by practically all cultures at all times. Egyptians, Chinese and, later, the Mayas produced their own synthetic turquoise analog, nowadays known as Egyptian blue, Han blue (or China blue) and Maya blue, respectively [7,8]. Porcelain, plastics, several copper and aluminum compounds, such as neolith (from Cu phosphate and $\text{Al}(\text{OH})_3$) and dyed howlite ($\text{Ca}_2\text{B}_5\text{SiO}_9(\text{OH})_5$) or magnesite (MgCO_3) were later used to imitate turquoise [9].

The list of simulants is long and includes ivory, calcite, glass and polystyrene resins [10].

Other minerals with similar color but with a totally different chemical composition (and commercial value) are often mistaken for turquoises. This is the case of chrysocolla ($\text{Cu}_{2-x}\text{Al}_x(\text{H}_{2-x}\text{Si}_2\text{O}_5)(\text{OH})_4 \cdot n\text{H}_2\text{O}$ with $x < 1$), a hydrated copper silicate and, more recently, faustite ($(\text{Zn,Cu})\text{Al}_6(\text{PO}_4)_4(\text{OH})_8 \cdot 4\text{H}_2\text{O}$) and blue prosopite ($\text{CaAl}_2(\text{F,OH})_8$) [11].

Currently, most gemstones are treated somehow but, due to the implications in the trade value, such procedures must be explicitly declared. Specifically in the case of turquoise, the treatments aim not only to improve the stone appearance but also its mechanical properties as to increase hardness and decrease porosity, as well as optical properties; such treatments can generally be classified as: (i) impregnation using oil or fats, in a procedure used since ancient times for making lapidary work easier and to provide the stone with a superior color and luster [1,12]; (ii) stabilization, made with epoxy, polystyrene or soluble glass (sodium silicate) this procedure uses chalky turquoise, which otherwise would be of no commercial use due to polishing difficult [1,4]; (iii) dyeing, generally with Prussian blue or more recently with metal phthalocyanines, for a more uniform color or even to hide some undesired apparent veins on the gem surface [10]; (iv) reconstitution made pressing turquoise powder and polishing wastes with a binding resin [10] and, less commonly, (v) gamma rays irradiation to render the stone less porous [13].

Considering that these treatments affect the stone value and in most cases are not identified by the naked eye, specific techniques are necessary to reveal the presence of chemical compounds or to

* Corresponding author at: Laboratório de Espectroscopia Molecular, Depto. de Química Fundamental – Instituto de Química, Universidade de São Paulo, Av. Prof. Lineu Prestes, 748 – Butantã, 05508-000 São Paulo, SP, Brazil. Tel.: +55 11 30913853. E-mail address: dlafaria@iq.usp.br (Dalva L.A. de Faria).

make evident the gem manipulation; such techniques are also used by gemologists for fake detection and encompasses non-destructive and destructive procedures. The first category is constituted by visual inspection with magnifying glasses, light absorption and density/refractive index measurements, whereas in the second are the microchemical tests, such as the use of a diluted HCl solution to reveal the presence of carbonates, or even the thermal decomposition of resins using a hot point [14]. Concerning the above cited non-destructive methods, they can be either not easy to use (as in the case of the light absorption spectrum by the gemstone), or not universally applied (refractive index measurement, for example) or the physical properties (refractive index and density) can be simulated by mixing different compounds. Furthermore, turquoise is a cryptocrystalline mineral, formed by the compact assembly of minute pseudo-rhombohedral crystals of hydrated copper and aluminum phosphate [15]. As a porous stone, it is not only vulnerable to substances that can affect its color (cosmetics, perfumes, etc.) but it is also prone to absorb oils and resins, compounds that are able to change its appearance and durability. It is thus evident the need of more precise and specific procedures.

Raman microscopy is being largely employed with forensic purposes, including the criminal aspects linked to gemology, such as fakes identification for example [16], since it is a non-destructive spectroscopic technique. It consists in the use of a white light microscope to illuminate the sample with a low power laser beam and to collect the light inelastically scattered by the sample. The intensity of the scattered light as a function of energy (given as wavenumber, cm^{-1}) is then plotted and used to fingerprint the compounds present in the probed area [17].

Reviews on the applications of Raman microscopy in gemology can be found in the literature [17–21] as well as an investigation on gems treatments [22], however, there is a lack of information concerning turquoises and only few reports were found. Raman microscopy was employed in the identification of turquoise from different sources [23,24], in the study of a resin used in a turquoise cabochon [22], in the characterization of odontolite used as a turquoise simulant [25] and in the investigation of the effect of pressure and impregnation on the mineral through the CH_2 , water and phosphate vibrations [26]. Salanne [27] made an extensive investigation of turquoise treatments and imitations by FT-Raman and SEM-EDS, however, the work is mostly based on minerals identification. Raman spectroscopy was also used together with UV–vis–NIR–IR spectroscopies and X-ray diffraction in the study of synthetic turquoises, however, the authors argue that the Raman spectrum is strongly affected by luminescence [28].

Considering the importance of turquoise as a gemstone, its relevance in cultural heritage objects and the relative scarcity of reference data on its fakes, Raman microscopy was employed in the characterization of allegedly turquoise stones, aiming at the identification of chemical compounds eventually used to mimic the gemstone or to enhance its mechanical or optical properties, thus contributing to the application of the technique in forensic sciences.

2. Materials and methods

2.1. Materials

Turquoise (Peru), chrysocolla (Peru), amazonite (Brazil), howlite (South Africa) and magnesite (Peru) were from a local stones dealer (Legem Mineração Ltda, Brazil); dyed howlite and a sample identified as “reconstituted turquoise” were also purchased from the same dealer (Table 1). All of them were analyzed as received. Copper and cobalt phthalocyanine (Sigma–Aldrich), cyanoacrylate glue (Superbonder™, 3M Brazil) were also used as reference substances. The analyzed adorns allegedly containing turquoise

Table 1

Investigated minerals with their respective chemical formula and main Raman bands (cm^{-1}).

Mineral	Chemical formula	Main Raman bands (cm^{-1})
Turquoise	$\text{CuAl}_6(\text{PO}_4)_4(\text{OH})_8 \cdot 4\text{H}_2\text{O}$	420 and 1040
Chrysocolla	$(\text{Cu}, \text{Al})_2\text{H}_2\text{Si}_2\text{O}_5(\text{OH})_4 \cdot n\text{H}_2\text{O}$	676
Amazonite	KAlSi_3O_8	475 and 511
Howlite	$\text{Ca}_2\text{B}_5\text{SiO}_{19}(\text{OH})_5$	328
Magnesite	MgCO_3	1009

were several pendants, beads and necklace from local Brazilian traders and an earring from Peru (unknown source). One certified cabochon from a local jewel manufacturer (Vivara, São Paulo, Brazil) was also investigated (Table 2). Pictures of the objects are provided as [supplementary material](#).

2.2. Methods and instrumental

The investigated samples and objects were analyzed by Raman microscopy directly on the microscope stage, without any manipulation or sample preparation. The spectra were obtained with the laser lines at 632.8 nm (He–Ne) and 785 nm (diode) with a Renishaw inVia Reflex Microscope fitted with a CCD Peltier cooled detector (Renishaw, 600×400 pixels) and a Leica optical microscope (DM2500 M); a $\times 50$ (N.A. 0.75) objective (Leica) was used in the measurements. Laser power below 0.5 mW at the sample was used in all the spectra obtained with visible excitation. FT-Raman spectra were recorded using a Bruker RFS 100/S fitted to a liquid nitrogen cooled Ge detector, working with spectral resolution of 4 cm^{-1} ; the 1064 nm line from a Nd^{3+} /YAG laser was used with the power being kept between 35 and 70 mW at the sample.

3. Results and discussion

Several minerals can be taken by turquoise, mostly due to their color, but because Raman spectroscopy is sensitive to chemical composition and structure, they are easily identified through their spectra as shown in Fig. 1, which depicts the spectrum of turquoise, chrysocolla and amazonite. The spectra (already reported in the

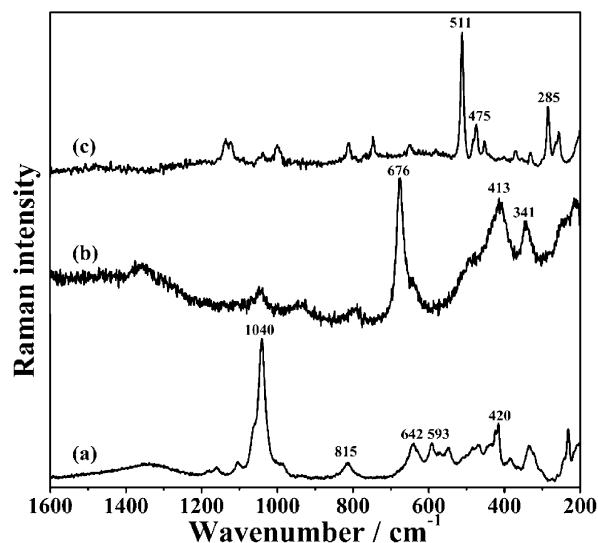


Fig. 1. Raman spectra of (a) turquoise (baseline corrected), (b) chrysocolla both obtained using $\lambda_0 = 785 \text{ nm}$ and (c) amazonite using $\lambda_0 = 632.8 \text{ nm}$ (baseline corrected). The 785 nm excitation was used when luminescence was present in the spectrum excited at 632.8 nm.

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