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A HISTORIC TURQUOISE JEWELRY SET CONTAINING FOSSILIZED DENTINE (ODONTOLITE) AND GLASS

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A set of six antique brooches, set with diamonds and light blue cabochons, was investigated with microscopy, Raman analysis, and EDXRF spectroscopy. Most of the cabochons proved to be fossilized dentine, also known as odontolite (mineralogically, fluorapatite). The brooches also contained turquoise and artificial glass.

The Swiss Gemmological Institute SSEF recently received a set of six antique brooches for identification (figure 1). These same pieces had already been presented in Bennett and Mascetti (2003, p. 102) as turquoise jewelry. They were set with numerous small rose-cut diamonds and a few larger old-cut diamonds, but most prominent were a number of light blue to greenish blue cabochons that appeared to be turquoise. Visual examination quickly revealed otherwise. Considering the historic background of these brooches, we were interested in examining the blue gems in greater detail to shed light on early turquoise imitations.

Turquoise, a copper-bearing hydrated aluminophosphate with the chemical formula $Cu(Al,Fe^{3+})_6(PO_4)_4(OH)_8 \cdot 4H_2O$, has been known since prehistoric times. It has been widely used in jewelry in the Middle East (Egypt and Persia), the Far East (Tibet, Mongolia, and China), and by native North Americans (Ahmed, 1999; Chalker et al., 2004). Yet turquoise was once very fashionable in Europe, especially during the 18th and 19th centuries (Bennett and Mascetti, 2003), so it is not surprising that imitations were used when genuine turquoise was not available. The wide range of turquoise imitations includes secondary minerals from copper deposits such as chrysocolla, dyed minerals such as magnesite or howlite, and artificial materials such as glass or sintered products (Arnould and Poirot, 1975; Lind et al., 1983; Fryer, 1983; Kane, 1985; Hurwit, 1988; Salanne, 2009).

In this study, we report on a historic turquoise substitute—fossilized dentine, also known as *odontolite*, *ivory turquoise*, *bone turquoise*, or *French turquoise*. Much of this material consists of fossilized mastodon ivory from Miocene-age (13–16 million years old) sedimentary rocks of the Gers District between the Aquitaine and Languedoc regions of southwestern France (Reiche et al., 2001). The tusks are hosted by alluvial sediments (molasse alternating with fine sand and clay facies) that accumulated in basins during the erosion of the nearby Pyrenees Mountains (Crouzel, 1957; Antoine et al., 1997). The fossilized dentine consists mainly of fluorapatite, $Ca_5(PO_4)_3F$; since medieval times, local Cistercian monks have used a heating process to turn the material light blue (de La Brosse, 1626; Réaumur, 1715; Fischer, 1819), which they thought to be turquoise. These "stones" were originally set in medieval religious artifacts, but came into fashion in the early to mid-19th century (Brown, 2007),

See end of article for About the Authors and Acknowledgment.

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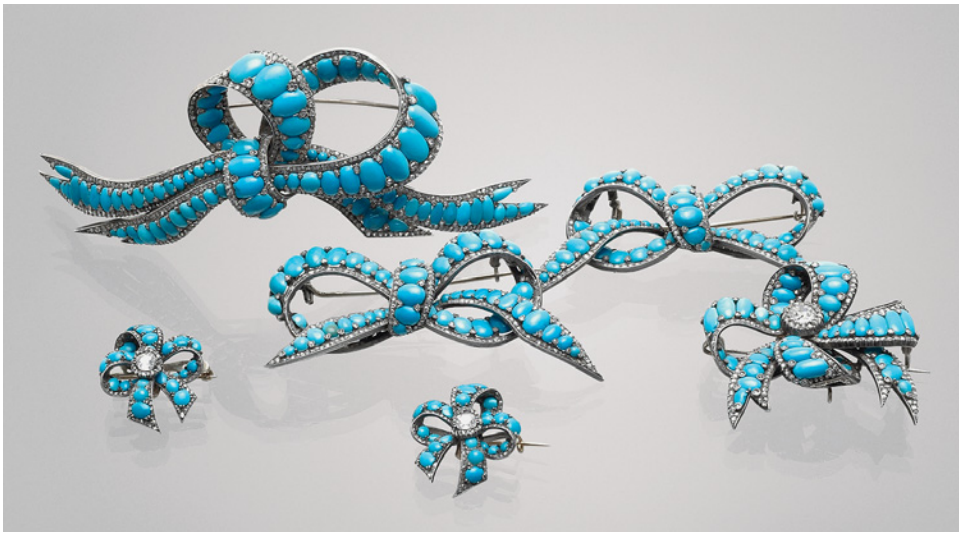


Figure 1. These six brooches are set with 313 light blue stones, the majority of which proved to be fossilized dentine (odontolite), mixed with a few turquoise and glass cabochons. Photo by Luc Phan, Swiss Gemmological Institute SSEF.

when fossilized dentine was recovered commercially in southwestern France.

A similar set of brooches containing odontolite was described by Crowningshield (1993). The present study offers further data on this material. Odontolite is rarely encountered in the market today, although it is occasionally present in historic jewels from private collections or museums. Gemologists seldom have the opportunity to test this material in the laboratory.

MATERIALS AND METHODS

Six brooches, all of very similar style (figure 1), were investigated. Their ornamental patterns of folded and knotted bands are characteristic of early to mid-19th century design (Bennett and Mascetti, 2003). Several French assay marks were seen on the metal mounting. In total, the brooches contained 313 opaque light blue cabochons from approximately 2 to 11 mm long, set with numerous small rose-cut diamonds and three old-cut diamond center-stones. The brooches ranged from approximately 2.5 to 14 cm long and from 6.6 to 53.6 g in weight.

All of the pieces were observed microscopically with 10–50× magnification. A few stones were very difficult to investigate due to the complexity of the mounting. Many of the cabochons were also examined at high magnification (200×) using an Olympus microscope coupled with our Renishaw Raman system. For identification, Raman spectra were taken on a large number of stones, using a 514 nm argon-ion laser (Hänni et al., 1998). The spectra were collected from 1800 to 100 cm^{-1} Raman shift, to include the vibrational range of organic compounds, such as wax and artificial resin, used for turquoise impregnation. In a few cases, spectra were collected up to 5000 cm^{-1} to check for OH bands in the dentine.

We also conducted semiquantitative energy-dispersive X-ray fluorescence (EDXRF) chemical analysis of two cabochons, using a Thermo Fisher Scientific Quant'X unit. These analyses, carried out using a series of excitation energies from 4 to 25 kV, covered a large range of elements, from Na to those with high atomic number.

RESULTS

The 313 light blue cabochons in the brooches (table 1) were categorized into three groups: odontolite (288

TABLE 1. Gems identified in the historic "turquoise" brooches.

Brooch	Location in figure 1	No. cabochons	No. analyzed by Raman	Odontolite[a]	Turquoise	Glass
A	Top left	94	88	87	7	0
B	Center	59	52	57	0	2
C	Top right	57	52	52	0	5
D	Bottom right	54	44	52	0	2
E	Bottom left	24	24	21	1	2
F	Bottom center	25	24	19	2	4
Total		313	284	288	10	15

[a] *Due to the mountings, a few of the odontolites could only be identified by microscopic examination; these are also included here.*

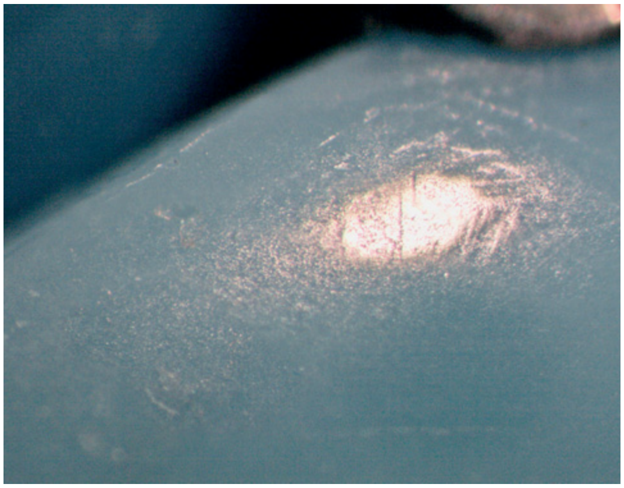


Figure 2. Micropores were observed on the surface of the odontolite cabochons. Photomicrograph by M. S. Krzemnicki; magnified 30×.

stones), turquoise (10), and artificial silica glass (15).

The odontolite cabochons all showed a micro-granular surface covered with a dense pattern of micropores. These very tiny pores were either rounded in outline (figure 2) or occurred as longitudinal channels, depending on how they were intersected by the curved surface of the cabochon. On a macro scale, these cabochons often showed weak banding (figure 3), and in some cases a very distinct pattern of curved intersection banding (figure 4), described as characteristic for elephant, mammoth, and mastodon ivory (Campbell Pedersen, 2010).

The Raman spectra of the odontolite revealed a distinct peak at 964 cm^{-1} and smaller peaks at about 1090, 580, and 430 cm^{-1} Raman shift (figure 5), and only a weak, broad OH band at about 3540 cm^{-1}. This pattern showed a perfect correlation with fluorapatite spectra taken from the SSEF reference mineral collection and with the published literature (Reiche et al., 2000; Campillo et al., 2010). EDXRF analyses of two cabochons confirmed their identity as apatite, revealing Ca and P as major elements and low concentrations of S, Cl, Sr, and Mn. Both analyses also revealed traces of Cu.

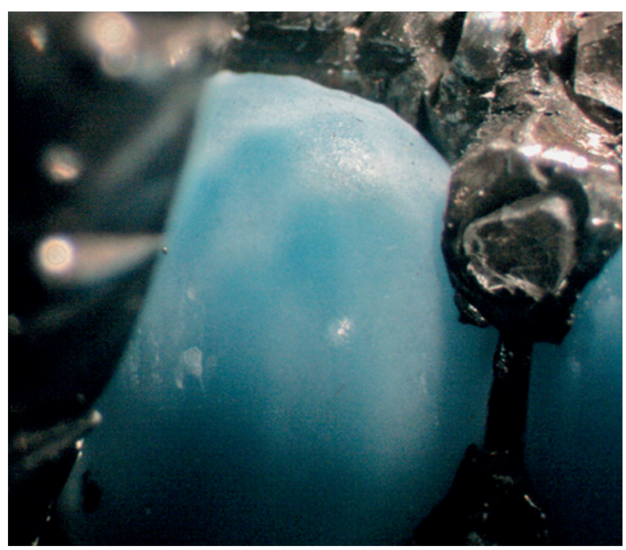
The turquoise cabochons showed a smoothly pol-

NEED TO KNOW

- Odontolite is fossilized dentine (mastodon ivory) from France that has been heat treated to produce its blue coloration.
- This historic turquoise substitute was identified in a set of six antique brooches set with diamonds.
- A combination of microscopic observation and Raman spectroscopy was effective for separating odontolite from the turquoise and artificial silica glass also present in the brooches.

Figure 3. The odontolite displayed weak banding. Photomicrograph by M. S. Krzemnicki; magnified 15×.

Figure 4. Characteristic curved intersection bands were visible on several of the odontolite cabochons. Photomicrograph by M. S. Krzemnicki; magnified 20×.



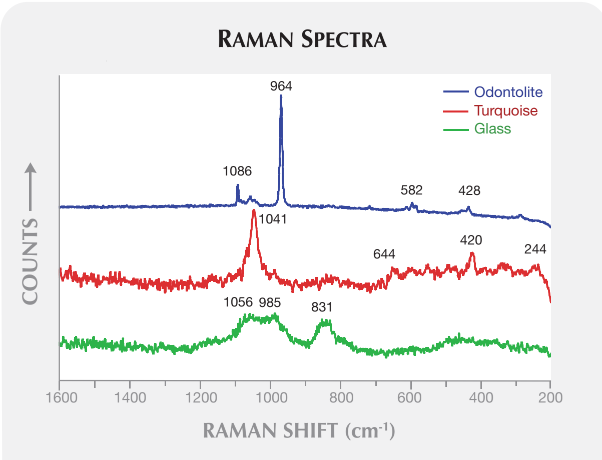


Figure 5. Raman spectra are shown for odontolite, turquoise, and blue silica glass.

ished surface and even color; some also had fine irregular brown veins (figure 6). They had a slightly more greenish blue color than the odontolite. Their Raman spectra were characterized by a general increase in Raman signal, with a distinct doublet at ~1040 cm^{-1} Raman shift and a series of smaller peaks between 650 and 200 cm^{-1}, typical for turquoise. We found no peak in the 1800–1400 cm^{-1} range that would be expected for turquoise treated with wax and/or stabilized with artificial resin (Kiefert et al., 1999).

The silica glass cabochons showed a smooth surface, with some scratches and small but distinctly spherical gas bubbles (figure 7). They revealed only a very weak, indistinct Raman signal characterized by three broad bands at about 1060, 985, and 830 cm^{-1}, attributable to the Si-O vibrational modes of silica glass (McMillan, 1984).

DISCUSSION

The brooches exemplify the fashionable use of odontolite as a turquoise imitation in mid-19th century period jewelry. This was especially true in France, the source of the material.

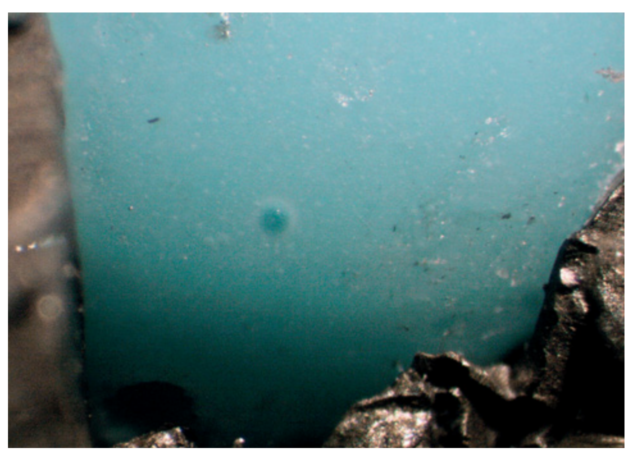
Figure 8 shows the distribution of odontolite and turquoise in the largest brooch. It contained only seven pieces of turquoise, together with 87 odontolite cabochons. The turquoise specimens were small and rather hidden, whereas the odontolite occupied the most prominent positions. In contrast to the other brooches, we found no silica glass in this item. In general, the distribution of turquoise cabochons in the brooches seemed rather random, and three of the

Figure 6. Fine brown veins are visible in this turquoise specimen. The two neighboring cabochons are odontolite. Photomicrograph by M. S. Krzemnicki; magnified 15×.

pieces did not contain any turquoise at all.

Bennett and Mascetti (2003, p. 89) pictured an antique brooch set with diamonds and blue cabochons described as odontolite and turquoise. One of the cabochons in the photo shows a distinctly greenish blue color, suggesting to the present authors that it is turquoise, mixed with seven odontolite cabochons. We presume that mixing of these similar-looking materials was common at that time. It is not clear how much the jewelers actually knew about the materials they were using.

Figure 7. A gas bubble is apparent in this glass cabochon in one of the brooches. Photomicrograph by M. S. Krzemnicki; magnified 25×.



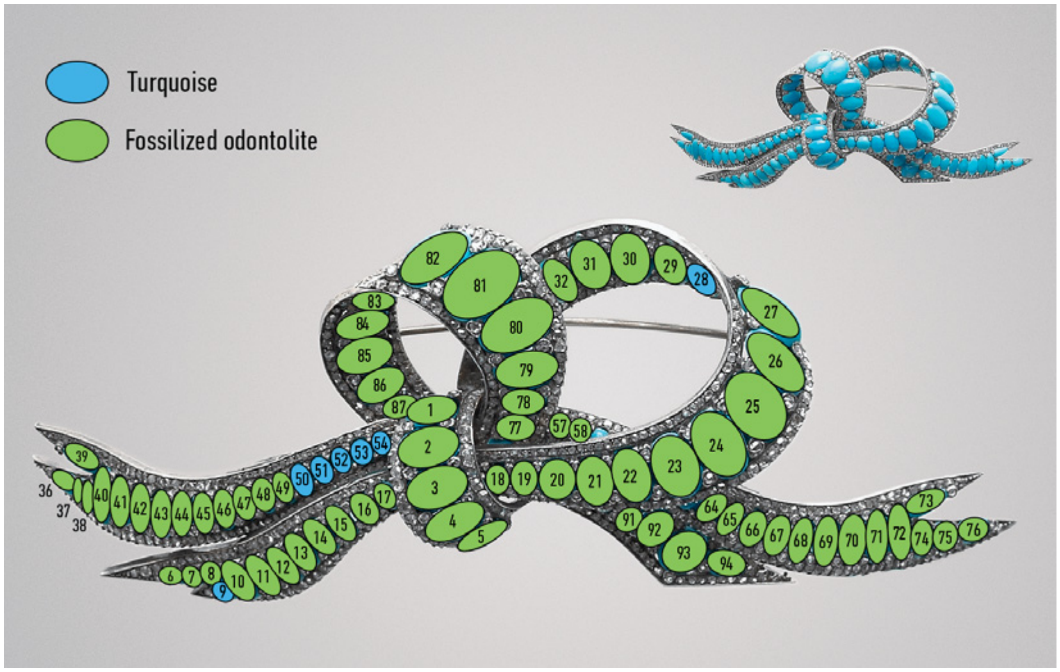


Figure 8. The largest brooch (~14 cm long) contained mostly odontolite with a few turquoise cabochons. Photo by M. S. Krzemnicki.

Based on its appearance and historical availability, we presume that the turquoise in this jewelry originated from classical sources in the Middle East, such as Persia. They showed no indications of any treatment (waxing, stabilization, or dyeing), as expected for the time period of the jewelry.

With its attractive light blue color, odontolite has been used as a turquoise simulant since the Middle Ages (Reiche et al., 2001). Although the heat-induced coloration was described in the early 18th century (Réaumur, 1715; Fischer, 1819), the cause of the blue color has been a subject of debate. Reiche et al. (2000, 2001) only recently showed that the oxidation of manganese traces within the fluorapatite during a heating process is responsible for the blue hue of the originally light gray odontolite. Using X-ray absorption spectroscopy, these authors found that heating to about 600°C under oxidizing conditions transforms octahedrally coordinated Mn^{2+} into tetrahedrally coordinated Mn^{5+}, which substitutes for phosphorous in the fluorapatite (Reiche et al., 2002).

The traces of Cu that we detected in the two odontolite cabochons using EDXRF spectroscopy may result from contamination during polishing. There was no visual indication on any of the investigated samples of artificial blue color concentrations, as would be expected for dyeing with a copper-bearing solution (e.g., copper sulfate).

The glass imitations were uncommon in these brooches. Whether they were set during the crafting or during subsequent repair is not known. Similar glass, however, has a long history as a substitute (Hänni et al., 1998), and is often found in fashion jewelry from the 19th century.

CONCLUSIONS

What started as routine testing of a set of brooches ultimately shed light on the widespread use of a rare turquoise imitation—odontolite—in mid-19th century jewelry that was much in fashion in Western Europe. The odontolite cabochons were mixed with turquoise and also set with glass either at the manufacturing stage or during subsequent repair. The most useful approach to identifying these materials is a combination of microscopic observation and Raman spectroscopy. Both methods are fully nondestructive so they can be readily applied to valuable historic objects.

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