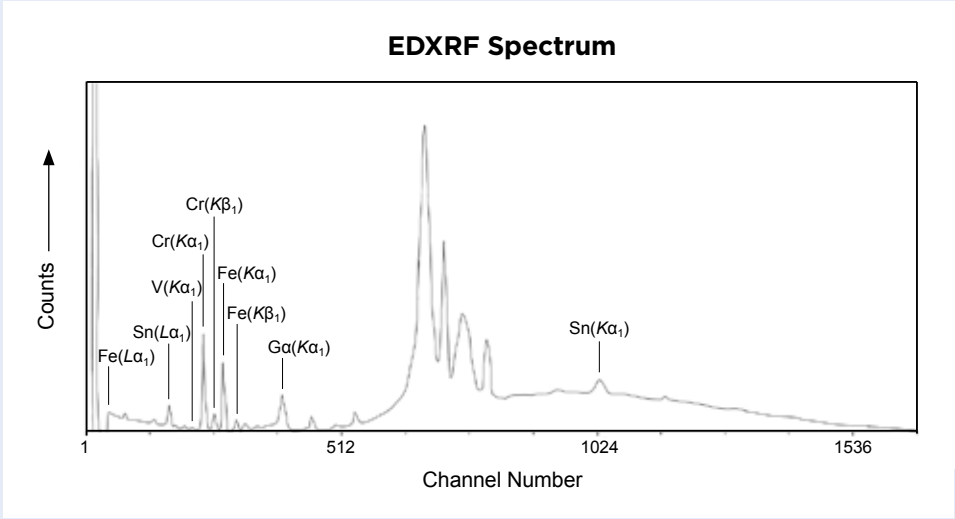

Figure 37: The EDXRF spectrum of the treated ruby reveals an anomalously high amount of Sn, as well as the presence of Cr, Fe, Ga and V. The large unlabelled peaks are instrumental artefacts.

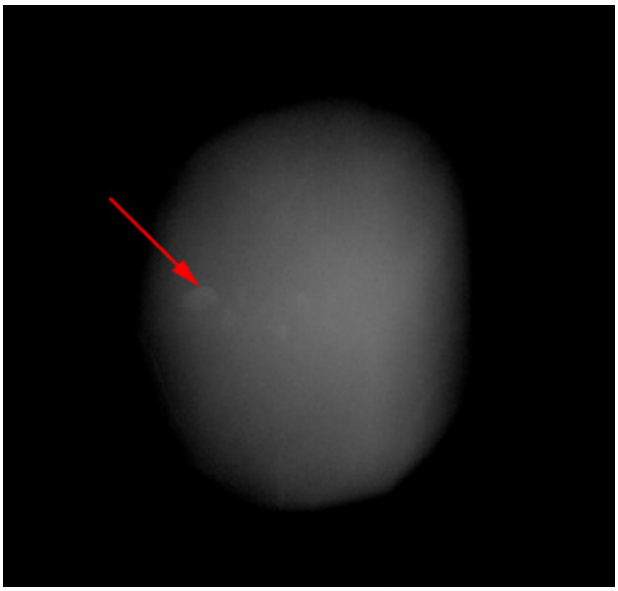

Figure 38: X-radiography of the 0.95 ct Sn glass-filled ruby reveals slightly lighter-appearing patchy areas (see arrow) corresponding to the location of the filler in surface-reaching fissures.

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A New Reconstructed Turquoise Imitation Composed of Turquoise Powder with a PMMA (Acrylic) Binder

The authors recently encountered a light greenish blue, slightly flexible, thin plate (about 0.8 ct; 5 × 7 × 0.3 mm), which we initially suspected to be stabilised turquoise. According to the client who submitted it, the material was intended for use in high-end jewellery, although we do not know if the initial supplier intended it for a particular application or if it was developed for a specific purpose (i.e. for mechanical or stability reasons). Some of its visual characteristics—in particular its homogeneity, lack of inclusions and glassy lustre (Figure 39)—suggested that it was not natural turquoise. Treatments of turquoise are well documented (e.g. Nassau 1994; Fritsch *et al*. 1999), and the use of organic compounds to stabilise such material has been extensively discussed in the literature (Moe *et al*. 2007; Han *et al*. 2015; Schwarzinger & Schwarzinger 2017). The major issues

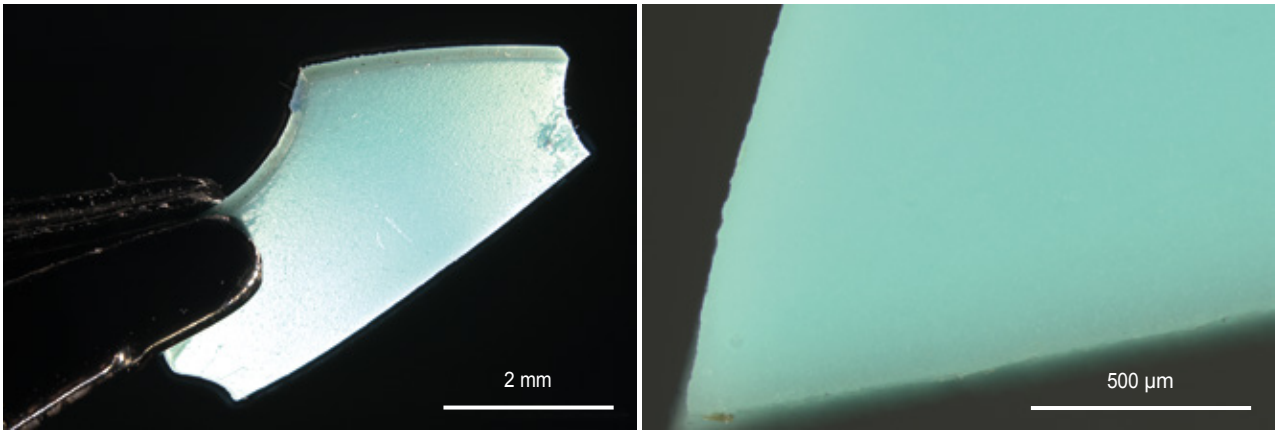

Figure 39: Microscopic examination of the turquoise-like specimen shows a glassy lustre (left) and extreme homogeneity, even at the highest available magnification (right). Photomicrographs by F. Blumentritt.

with turquoise are its low lustre and hardness (mainly due to high porosity) and its colour instability (Nassau 1994), which can be minimised by coating with epoxy resin or by injecting a plastic filler into the pores in a vacuum (to remove the air) or under pressure (to push in the filler; Moe *et al.* 2007).

In the present sample, fractures along the edges of the piece appeared relatively smooth compared to those typically seen on turquoise, and the absence of any colour concentrations around fractures excluded the possibility of dyeing (Fritsch *et al.* 1999). Further observations at the highest available magnification of our optical microscope (160×) did not help with determining the nature of the specimen due to its extreme homogeneity (again, see Figure 39). The sample was, unfortunately, not large enough to measure an accurate SG, although this measurement could have been useful for characterising the material, as organic compounds very often have a much lower SG than turquoise (2.6–2.8). The RI was recorded as about 1.55, which is lower than expected for untreated turquoise (about 1.62; Webster 1994).

Specular reflectance infrared spectroscopy showed features consistent with turquoise, along with some minor differences, which we attributed to possible impregnation treatment (Dontenville *et al.* 1985) or a surface coating. EDXRF chemical analysis revealed a composition matching that of turquoise, including the usual minor and trace elements, such as Zn, Sc and As (e.g. Khorassani & Abedini 1976; Fertelmes & Loendorf 2012).

The Raman spectrum (532 nm laser excitation, 10 mW) revealed turquoise signals, as well as the presence of an organic compound identifiable by sharp, intense features around 3000 cm^{-1} (CH_2 and CH_3 vibration modes; Figure 40). These bands are similar to those recently observed in treated turquoise from Armenia (Štubňa & Andrášiová 2021). Among the large list of possible compounds, we determined that the Raman features correspond best to the acrylic material known as *poly(methyl methacrylate)*, or PMMA (e.g. Plexiglas).

Scanning electron microscopy (SEM; using a JEOL 7600 instrument) was then conducted to determine whether the PMMA was used as a stabiliser for massive porous turquoise or as a binder for turquoise powder. The image in Figure 41 shows disordered tabular grains of turquoise that are up to several micrometres long. They are integrated into an organic matrix that represents at least 20% by volume (estimated visually) of the material. This demonstrates that the material consists of fine grains of turquoise embedded in a matrix of PMMA (as identified above by Raman spectroscopy).

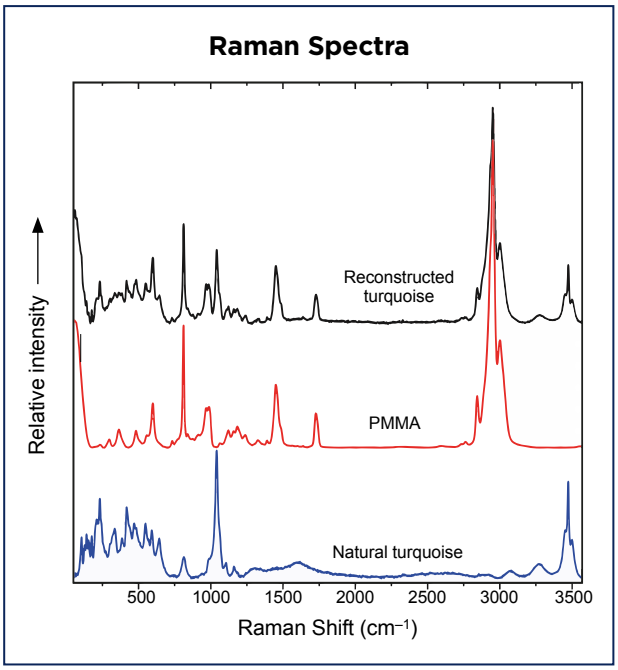

Figure 40: The Raman spectrum of the sample is consistent with a mixture of poly(methyl methacrylate), or PMMA, and natural turquoise.

This conclusion is supported by our other observations, such as the thin plate's homogeneity, glassy lustre and slight flexibility.

Assuming that the mixture of turquoise and PMMA is relatively homogeneous, then the amount of PMMA in such a mixture can be calculated from the sample's RI with the following equation: $1.55 = 1.49x + 1.62(1-x)$ using, respectively, the RI values of 1.49 for PMMA (Speight 2005) and 1.62 for turquoise (Webster 1994). This yields a proportion of 54% PMMA. Although this value does not correlate well with the visual impression of the sample's surface as seen with the SEM (>20% PMMA), a three-dimensional image of the volume would be needed to estimate it correctly, because the incident electron beam more easily penetrates PMMA than turquoise. Consequently, the presence of PMMA is not as well visualised when there is turquoise just below a PMMA layer that is not thick enough to prevent electrons from passing through it. However, this value reflects the covering of turquoise grains by PMMA at the surface of the plate and confirms the extensive use of organic binder in this material.

The similar practice of cementing together turquoise fragments with some sort of organic material has been mentioned occasionally in the literature (Lee & Webster 1960; Moe *et al*. 2007; Choudhary 2010). In those articles, the organic substance was defined as 'plastic', 'polymer' or 'epoxy resin' without being more specific. Hence, to the authors' knowledge, the use of PMMA to produce reconstructed turquoise using natural stone powder has not been documented previously in the gemmological literature.

This new reconstructed turquoise imitation could be quite challenging for gemmological laboratories since, without SEM imaging, it could be easily confused with impregnated turquoise. At present, when PMMA is identified in turquoise by Raman spectroscopy, the authors recommend estimating the amount of filler from the RI and SG values, and calling it *reconstructed* in the case where it is estimated that there is more than 20% PMMA. If there is less than 20% PMMA, the material should be referred to as *stabilised* (while specifying that PMMA is used as the stabiliser). Simple tests with heat, fire or solvents might be helpful for laboratories or suppliers wishing to verify whether a sample is impregnated or reconstructed. However, such testing is (micro)destructive, and correlating the resulting reactions with the amount of filler present would need further study.

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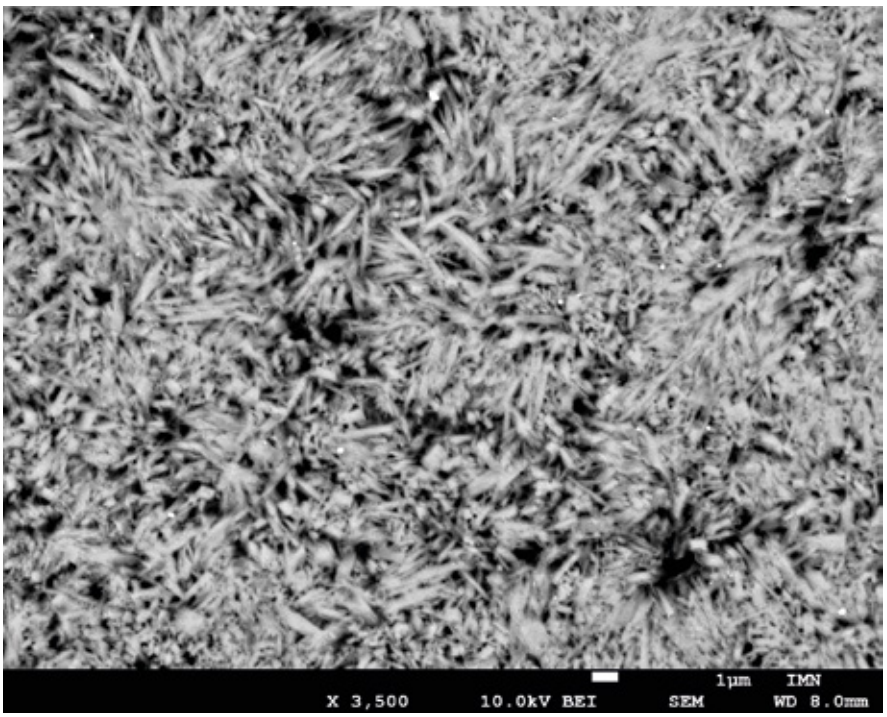

Figure 41: In this SEM image of the surface of the sample, use of a backscattered-electron detector, which reflects the chemical composition of the material, shows the global disorder of the turquoise grains (light tones) that are cemented together with organic matter (dark tones). Image by N. Stephant and E. Fritsch.

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