Simulated Malachite with Barium Sulphate as the Major Constituent
硫酸鋇為主要成分的孔雀石模擬石

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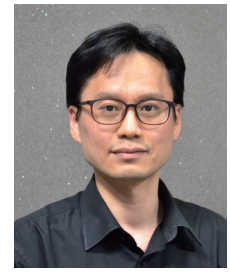

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一顆具有深、淺綠色的（樣品A），重7.13cts，並有黑色條紋的蛋面形寶石被提交給韓國Wooshin寶石學院(WGK)進行鑑定服務(Fig. 1； A1和A2)。孔雀石($Cu_2(CO_3)(OH)_2$)是一種觀賞寶石，因其獨特的顏色和彎曲或直條紋圖案而備受喜愛。提交給WGK的樣品(A)的外觀類似孔雀石，其帶狀輪廓不規則（粗糙），並且其外觀與天然孔雀石略有不同(Fig. 1)。因此，初步推測它是重構的孔雀石或塑料仿製品，但經檢查證明它是由硫酸鋇製成的孔雀石模擬石。

Introduction

A light green, cabochon-shaped stone (sample A) with dark green and black stripes weighing 7.13 cts was submitted to the Wooshin Gemological Institute of Korea (WGK) for identification (see Fig. 1; A1 and A2). Malachite $Cu_2(CO_3)(OH)_2$ is an ornamental gemstone that is loved for its unique colour and curved or straight striped patterns. The sample (A) submitted to WGK has an appearance similar to that of malachite, but the band outline is irregular (rough) and it looks slightly different from

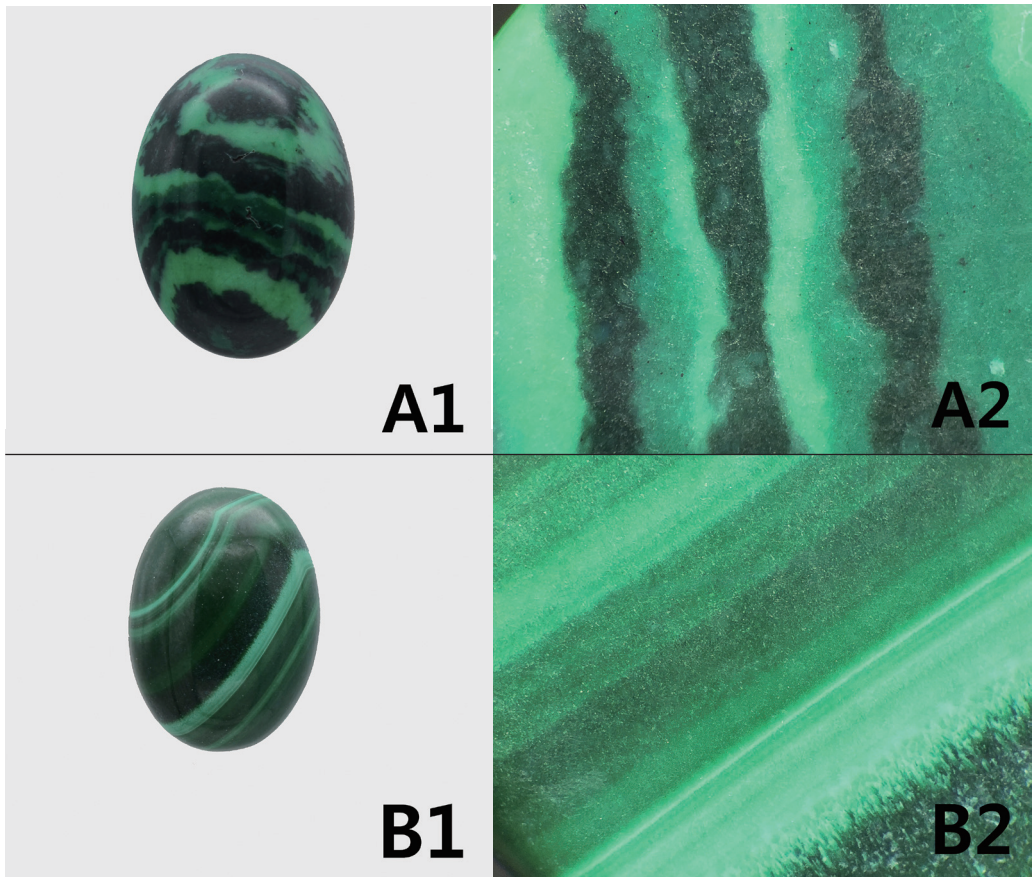

Fig. 1 A view of sample A imitating malachite (A1) and a natural malachite (B1). Close-up of the band outline of the two stones (A2, B2). *Photo © Wooshin Gemological Institute of Korea*
樣品A孔雀石模擬石(A1)和天然孔雀石(B1)。兩顆石的條紋放大圖 (A2, B2)。

natural malachite (Fig. 1). Because of this, it was presumed to be reconstituted malachite or a plastic imitation, but examination revealed that it was a malachite imitation made from baryte (also called “barite” or “barium sulphate”) .

Testings

Gemmological properties

Sample A was a cabochon cut stone with a refractive index (RI) of 1.63(s) and a specific gravity (SG), obtained hydrostatically, of 2.23. Natural malachite has a SG of 3.6-4.05. Standard gemmological testing of the natural malachite revealed an RI of approximately 1.656 - 1.909 and sample A showed a large birefringence of 0.254 (see Table 1). Because sample A was measured by the spot method, it was not possible to measure the birefringence accurately. Malachite’s birefringence is large so that a birefringence blink can be observed when measuring the refractive index, but this was not seen in sample A. In addition, malachite does not generally have an ultraviolet fluorescence reaction, but sample A showed a strong fluorescence (weak fluorescence reaction even at short wavelengths) in the longwave ultraviolet; a discernible difference (Fig. 2).

Properties	Sample A	Natural Malachite
Refractive Index (RI)	1.63 (spot reading)	1.655 - 1.909
Specific Gravity (SG)	2.23	3.95
Ultraviolet Fluorescence	SW : Weak LW : Strong	SW / LW : None

Table 1. A comparison of the gemmological properties of the two stones.
兩件寶石的寶石學性質對比

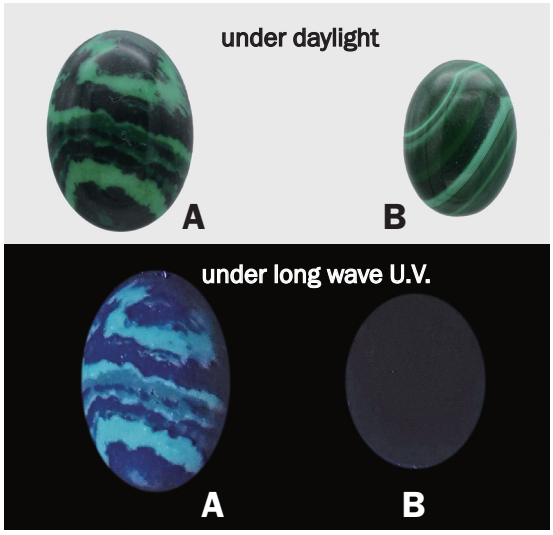

Fig. 2 Sample A exhibited a strong fluorescence to longwave U.V. A: Sample A; B: natural malachite
Photo © Wooshin Gemological Institute of Korea
樣品A對紫外線長波顯示強熒光。
A：樣品A，B：天然孔雀石

The SG of natural malachite is 3.25 to 4.10, but the SG of sample A is 2.23, which is different from that of natural malachite (Table 1). Synthetic malachite also has the same physical, chemical, and optical properties as the natural stone, so its refractive index and specific gravity are much the same as those of the natural stone (Bublikova, 2019 and Chernenko, 2003). It was recognised that if Sample A was reconstituted malachite, it could well have a lower specific gravity than natural malachite because such imitations are mixed with polymer. The submitted stone also showed a difference from the specific gravity of plastic (1.25 ~ 2.00) (Density of Plastics: Technical Properties). In the case of simple plastic, when a strong light is shone on a thin part of the edge, some light transmission is observed, but this submitted stone did not show any light transmission.

Chemical analysis and Infrared Spectrum

Using standard gemmological testing, it was confirmed that the submitted stone showed different results from natural or synthetic malachite. To confirm whether it was reconstituted malachite, we performed qualitative EDXRF chemical analyses with an EDX-8000 instrument (Shimadzu) and FT-IR measurement with Nicolet iS-50 (Thermo

Oxide Composition	Submitted Stone	Natural Malachite	Natural Baryte
BaO	53.521	-	56.006
SO_3	37.149	-	43.886
Al_2O_3	4.850	-	-
SiO_2	2.140	-	-
CaO	1.246	-	-
SrO	0.662	-	0.108
K_2O	0.144	-	-
ZnO	0.148	-	-
CdO	0.072	-	-
CuO	0.067	100	-

wt%

Table 2 The results of the chemical analyses of the submitted stone, natural malachite, and natural baryte.
提交予檢測的石材、天然孔雀石和天然重晶石的化學分析結果對比。

Scientific). As shown in Table 2, analysis of the main components of Sample A were shown to be barium and sulphur. Very little copper, the major component of malachite, was detected (Balitsky, 1987, Breeding010, and Synthetic malachite producing method).

According to the data (Koivula, 1991 and 1992), imitation malachite is produced by mixing baryte and gibbsite or by using barium sulphate and resin as a binder. Through chemical analysis of the sample, the main components of baryte were confirmed, and the ATR-FT-IR (Lumos, Bruker) measurement results, verified it as baryte with the results as the chemical analysis.

In Fig. 3, absorbance peaks at 1180, 1063, 991 cm^{-1}, and 634, 603 cm^{-1} indicate baryte, and 1560, 1497, 1345, and 813 cm^{-1} represent the resin component melamine-urea-formaldehyde resin (MUF Resin). Other 2906, 2836, and 1725 cm^{-1} peaks are judged to be wax components (Database of ATR-FT-IR spectra of various materials and Moe, 2007).

It is speculated that SiO_2, CaO, SrO, etc., other than the main components of baryte, are minor components in the baryte mineral as a raw material or are additive components for making imitation stones. In the case of Al_2O_3, further testing was needed to determine whether it was due to impurities or an admixture of Gibbsite.

Raman Spectroscopy Analysis

Among the malachite imitation stones using baryte, Raman measurement with Qontor (inVia Raman spectroscopy, Renishaw) was performed to distinguish whether the sample was an imitation stone made by mixing baryte and gibbsite with resin or a baryte and resin imitation stone. In Fig. 4, the presence of baryte was confirmed through 987, 453, and 462 cm^{-1} peaks, but as a result of several measurements on the different points, the Raman peak that could confirm the presence of Gibbsite was not found. Al_2O_3, which was detected in the chemical analysis, is presumed to be incorporated or one of other additive components. Other peaks are dyes mixed with resin. The feature at 1539, 779, 740, and 685 cm^{-1} peaks that were present in the Raman spectra of this copper phthalocyanine (Carlos, 2017) and 978 cm^{-1} was reported as the resin's triazine ring (Magnusson, 2015) (see Fig. 4). Therefore, it was revealed that this submitted stone could be showing a mixture of dye and resin.

Conclusion

So far, comprehensive analysis results suggest that sample A is a malachite imitation made by mixing barium sulphate, dye, and melanin resin. It may be referred to as plastic if viewed broadly, but is different from a simple plastic imitation stone. The SG value of 2.23 reveals clearly that

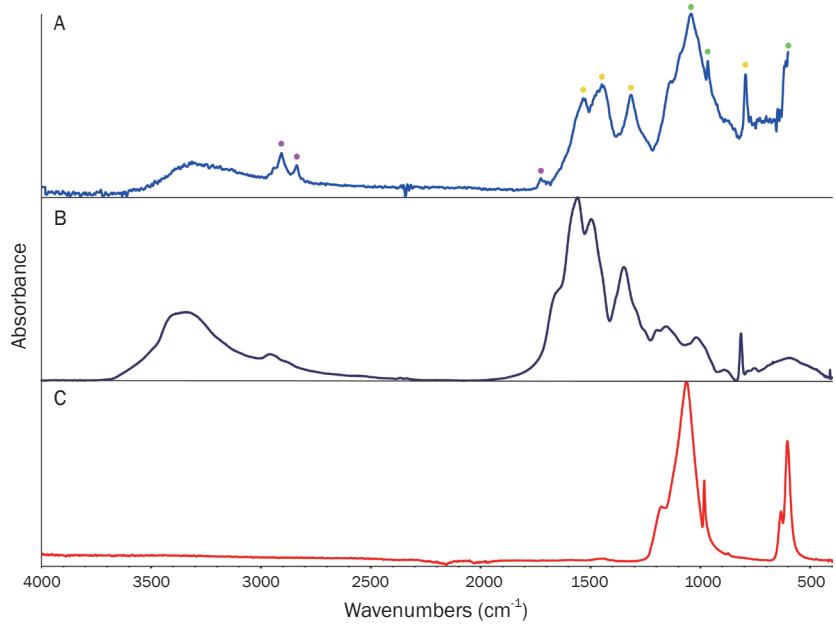

Fig. 3 The mid-infrared spectra of (A) sample A, (B) melamine-urea-formaldehyde (MUF, Omnic library data), and (C) baryte (RRUFF data).
(A) 樣品A，(B) 三聚氰胺-脲-甲醛（MUF，Omnic庫數據）和 (C) 重晶石（RRUFF數據）的中紅外光譜。

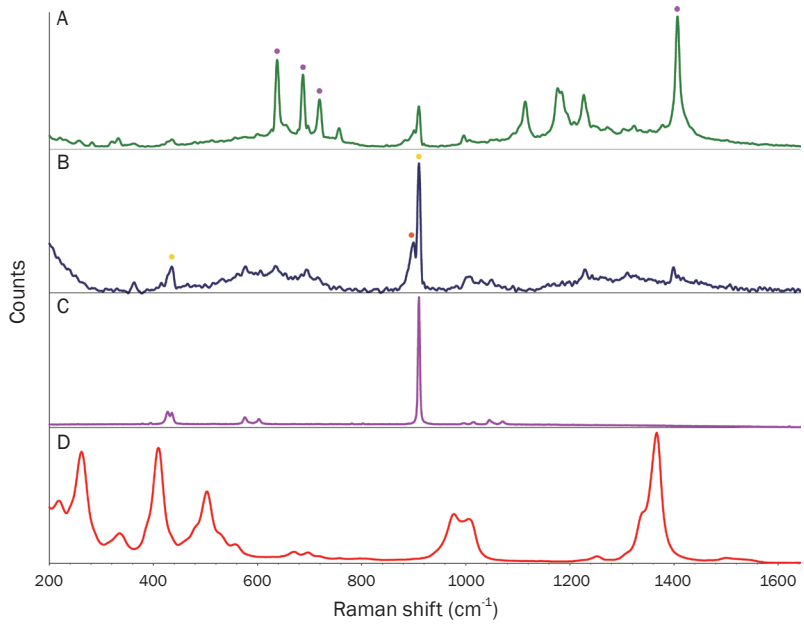

Fig. 4 Comparison of the Raman spectra results of natural baryte and Sample A. Spectra (A) and (B) are the from Sample A measured at different points. Spectrum (C) is baryte, and spectrum (D) is malachite (RRUFF data, RRUFFID=R050508).
天然重晶石和樣品A的拉曼光譜結果的比較。光譜 (A) 和 (B) 是樣品A在不同射測點測得的光譜，光譜 (C) 是重晶石，光譜 (D) 是孔雀石（RRUFF數據，RRUFFID = R050508）。

the material cannot be malachite. Baryte is a mineral that becomes the raw material of barium sulphate if it is transparent and of high quality and is polished and used for jewellery. When synthetic barium sulphate is used with a polymer filler, chemical resistance is increased, and its high refractive index. Therefore, this malachite imitation is more resistant to heat and chemicals than ordinary plastics would be and it will not discolour. It is considered to have baryte as its main component to give it a high lustre similar to jewellery grade stones. Another straight forward method of distinguishing this imitation from malachite would be an energy dispersive X-Ray fluorescence analysis where the absence of copper as the main constituent would also demonstrate the difference.

Acknowledgements

The author would like to thank Hye-Soo Kim and Jung Soo Min for the photos and graphics in this article.

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