LA-ICP-MS Analysis as a Tool for Separating Natural and Synthetic Malachite

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Malachite ($Cu_2[(OH)_2|CO_3]$) is a popular ornamental gemstone well known for its strong green color and banded growth pattern (figure 1). Although individual stones are not generally very high in value, malachite is widespread in the jewelry market and often sold in bulk. The quantity of material available creates urgency for gem laboratories to be able to conclusively separate natural and synthetic samples.

Gem-quality natural malachite has been mined from many different localities, including notable deposits in the Congo (formerly Zaire) and the Ural Mountains of Russia and Kazakhstan. Synthetic malachite was introduced in the late 1980s by Russian scientists experimenting with precipitation of the hydrous copper carbonate from aqueous solutions (figure 2). In appearance, structure, and composition, the lab-grown samples were very similar to their natural counterparts. It is unclear how long the production of the synthetic material continued, but currently there are no known producers. This material was documented at the time by Balitsky et al. (1987).

Gemologists have not taken great pains to separate natural and synthetic malachite, mainly due to a lack of conclusive identification features. LA-ICP-MS analysis has become popular in the gem industry because of its high sensitivity for measurement of trace elements in gemstones. It has been used successfully for country-of-origin determination for rubies, sapphires, emeralds, and copper-rich tourmaline, as well as the separation of natural and synthetic corundum and quartz. We applied this technique to malachite in an attempt to make the separation using trace-element chemistry.

Nine samples of natural malachite from unknown localities, including those shown in figure 1, and five samples of synthetic malachite shown in figure 2, were analyzed using a Thermo X-Series II ICP-MS instrument combined with a New Wave 213 nm laser-ablation sample introduction system. Laser operating conditions included a 7 Hz repetition rate, 40 µm spot diameter, ~ 2 J/cm^2 fluence, and NIST glass standards. Helium was used as the carrier flow gas to transport the ablated sample into the ICP-MS. Multiple spots were run on each sample and averaged to minimize sample heterogeneity.

The LA-ICP-MS analysis results showed very clearly that Zn and Mg occurred in higher concentrations in the synthetic samples, while Co and V were enriched in the natural malachite (figure 3). Even more striking were the differences noted for Be, P, and Ni concentrations (table 1). Ni occurred in concentrations nearly three orders of magnitude higher in the synthetics. Conversely, Be and P were detected in all of the natural samples, but were below detection limits in the synthetics. These results clearly indicate that natural and synthetic malachite can be separated on the basis of trace-element chemistry

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and that LA-ICP-MS analysis is an extremely valuable tool for this determination. The limited number of available samples means that more work is needed to confirm the results, but the potential for using this technique appears very high.

Reference

Balitsky V.S., Bublikova T.M., Sorokina S.L., Balitskaya L.V., Shteinberg A.S. (1987) Man-made jewelry malachite. *Gems & Gemology*, Vol. 23, No. 3, pp. 152-157.

Figure 1. Natural malachite, like the analyzed material shown here, is well known for its bright green color and distinctive banded structure.

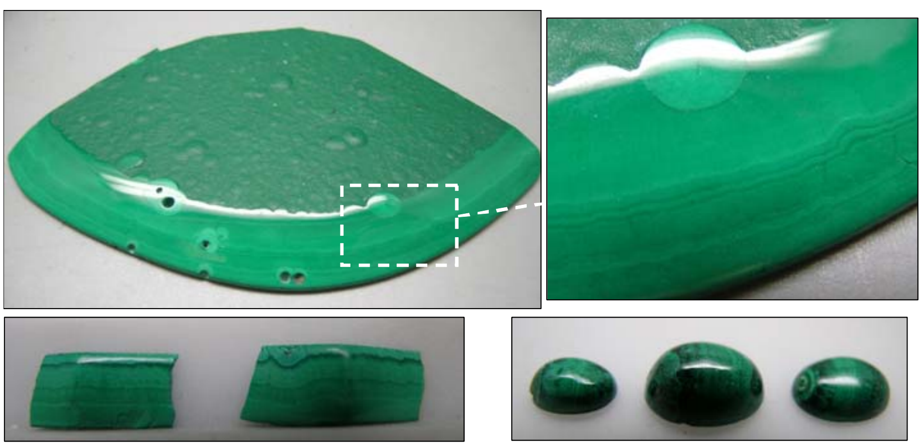

Figure 2. Synthetic malachite was grown from aqueous solutions in Russia starting in the 1980s. Its color, texture, and overall appearance are nearly identical to natural malachite. The five samples in the bottom photos were analyzed for this study.

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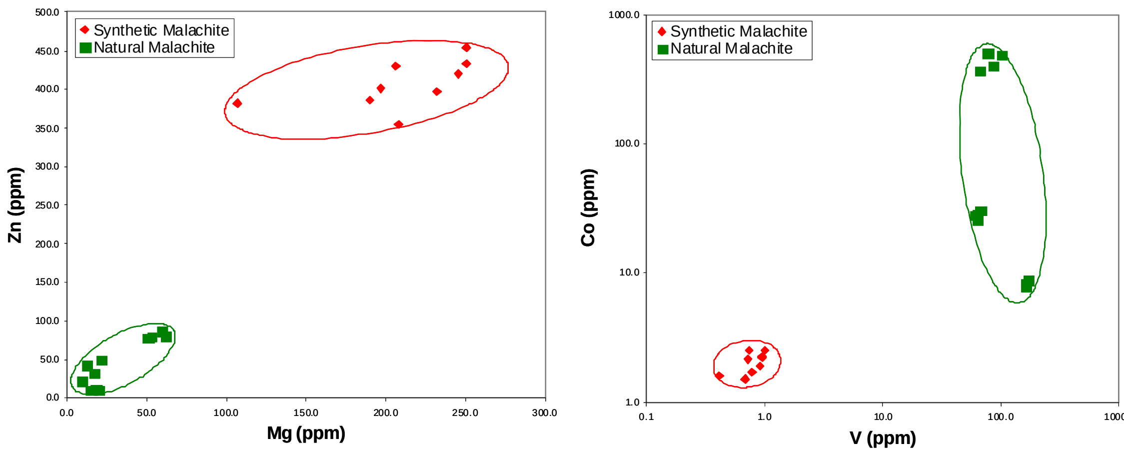

Figure 3. These chemistry plots clearly show the enrichment of Zn and Mg in synthetic malachite and elevated concentrations of Co and V in natural samples. Note that the Co and V data are plotted in log scale for clarity.

Sample		Be	P	Ni
		ppm	ppm	ppm
Synthetic	CB00023	bdl	bdl	15150
	CB00024	bdl	bdl	17700
	CB00025	bdl	bdl	11790
	CB00026	bdl	bdl	5325
	CB00027	bdl	bdl	3650
Natural	CB00028	7.8	3880	bdl
	CB00029	19.4	4810	21
	CB00030	36.7	3890	53
	CB00031	4.1	1340	30
	CB00032	4.1	487	12
	CB00033	6.3	644	24
	CB00034	6.1	1680	11
	CB00035	8.8	3890	36
	CB00036	20.1	5160	46

bdl = below detection limits
All sample data consist of an average of 2-4 spot analyses.

Table 1. These data show the significantly elevated concentrations of Ni in synthetic malachite samples and the presence of Be and P only in natural samples. These obvious differences make separation relatively straightforward with trace-element analysis.