Natural-Colored Chrome Chalcedony Identified Using Laser Ablation–Inductively Coupled Plasma–Mass Spectrometry (LA-ICP-MS)

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Recently, Mr. Shun-Tien Ten Wu of Taiwan sent the author a sample of unpolished blue-green rough material weighing approximately 79 ct (~36 mm × 20 mm × 16mm) for scientific examination (figure 1). The stone was reportedly from Indonesia and suspected to have been dyed. After reading the GIA Laboratory's study on the identification of dyed chrysocolla chalcedony using ultraviolet-visible-infrared (UV-Vis-IR) absorption spectroscopy (Shen et al., 2006), Mr. Wu allowed us to cut a 20 × 16 × 1.5 mm slab from the sample for analysis. Macroscopic observation revealed bands of various colors ranging from bluish green to green to near-colorless. Viewed under magnification, the specimen displayed the rolling flow structure that is typical of chalcedony, with color concentrations along some of the bands and near one edge (figure 2). Its specific gravity (2.568, measured hydrostatically) and refractive index (1.54) were consistent with published values for chalcedony.

Qualitative energy-dispersive X-ray fluorescence (EDXRF) spectrometry indicated that Cr, Ni, and Fe were the only significant trace elements in the sample. The glaring absence of Cu indicated that the stone was not colored by minute chrysocolla inclusions, as described in Shen et al. (2006). In the IR region, the absorption spectrum (figure 3) from the 1.5 mm thick slice showed the common ~1400, ~1900, and ~2300 nm broad bands related to the hydroxyl group in chalcedony and opal (see Shen et al., 2006). But in the visible range (400–750 nm), the absorption features of this sample were very different from those of chrysocolla chalcedony. This sample showed two strong absorption bands (414 and 594 nm) rather than the single broad band (527–1176 nm) seen in chalcedony that contains Cu^{2+}. These two strong absorption bands are identical to previously published chrome chalcedony spectra (Hyrsl, 1999). Therefore, the spectrometric method used in Shen et al. (2006) cannot be applied to this particular stone at all. In fact, a sample with such uneven color distribution often generates inconclusive results with spectrometric methods.

The presence of the various color bands, however, provided an excellent opportunity to evaluate the source of the coloring agent for this particular sample. Unlike the bulk analysis provided by many EDXRF instruments, laser ablation–inductively coupled plasma–mass spectrometry (LA-ICP-MS) is capable of analyzing a very small area (micrometer-scale) and providing detailed information about how elements are distributed in an unevenly colored sample such as this one. In addition, LA-ICP-MS is capable of detecting almost every element in the periodic table. Using a Thermo X-series II ICP-MS equipped with a New Wave UP-213 laser ablation unit (~8 J/cm^2 fluence, 7 Hz repetition rate), we collected data from a series of analysis spots (40 and 55 µm diameters) across the 1.5 mm thick slab, making sure to include all color zones. A total of 56 spots were analyzed, 28 of which were performed with each laser spot diameter setting. The spots covered the entire color profile of the sample, from the white opaque area at the top right in figure 4 to the white translucent area at the bottom right of same figure. Figure 5 shows a close-up of the top right corner of the sample, where two vertical columns (40 µm spots to the left, 55 µm to the right) of ablation pits are clearly visible.

Figure 6 shows a plot with a selection of nine elements measured across the profile: Mg, Al, K, V, Cr, Fe, Cu, Ga, and Ni. These elements showed highly correlated variation patterns throughout the sample. Chalcedony is widely documented as forming by multiple-stage growth from hydrothermal fluids (see Heany, 2005 and the references therein). Each growth increment may involve fluids of similar or different trace-element compositions. This variation in trace-element concentrations often results in multiple colors in a single piece of chalcedony (Michalski and Foord, 2005). In Mr. Wu's sample, the fact that the trace elements show such a strong correlation with each other means that they were all incorporated in the chalcedony at the same time (i.e., during growth) and the color of the material was likely never altered by a treatment involving dye. If dye had been introduced, it would be very difficult to maintain such a consistent correlation between Cr (the main coloring agent in this case) and the other trace elements. Instead, one would expect noticeable spikes or plateaus in Cr content in areas where dye might produce color concentrations. This technique can be applied to many other gem materials that are suspected of having been dyed, because the trace-element fingerprint is very sensitive to foreign substances.

Because LA-ICP-MS analysis is much more expensive and complicated to perform, however, a spectroscopic method should be the first choice. If LA-ICP-MS analysis is warranted, fewer sampling spots (10, for instance) may yield satisfactory results. The results of ongoing research using this technique to evaluate chrysocolla chalcedony will appear in a future paper in *Gems & Gemology*.

References

Heany P.J. (2005) A proposed mechanism for the growth of chalcedony. In D. Kile, T. Michalski, and P. Modreski, Ed., *Symposium on Agate and Cryptocrystalline Quartz: Program and Abstracts*, pp. 139–144.

Hrysl J. (1999) Chrome chalcedony – A review. *Journal of Gemmology*, Vol. 26, pp. 364–370.

Michalski T.C. and Foord E.E. (2005) Seven causes of color in banded agate. In D. Kile, T. Michalski, and P. Modreski, Ed., *Symposium on Agate and Cryptocrystalline Quartz: Program and Abstracts*, pp. 60–66.

Shen A., Fritz E., DeGhionno D., and McClure S. (2006) Identification of dyed chrysocolla chalcedony. *Gems & Gemology*, Vol. 42, No.3, p. 140.

Figure 1. This piece of rough chrome chalcedony (~79 ct) is believed to be naturally colored.

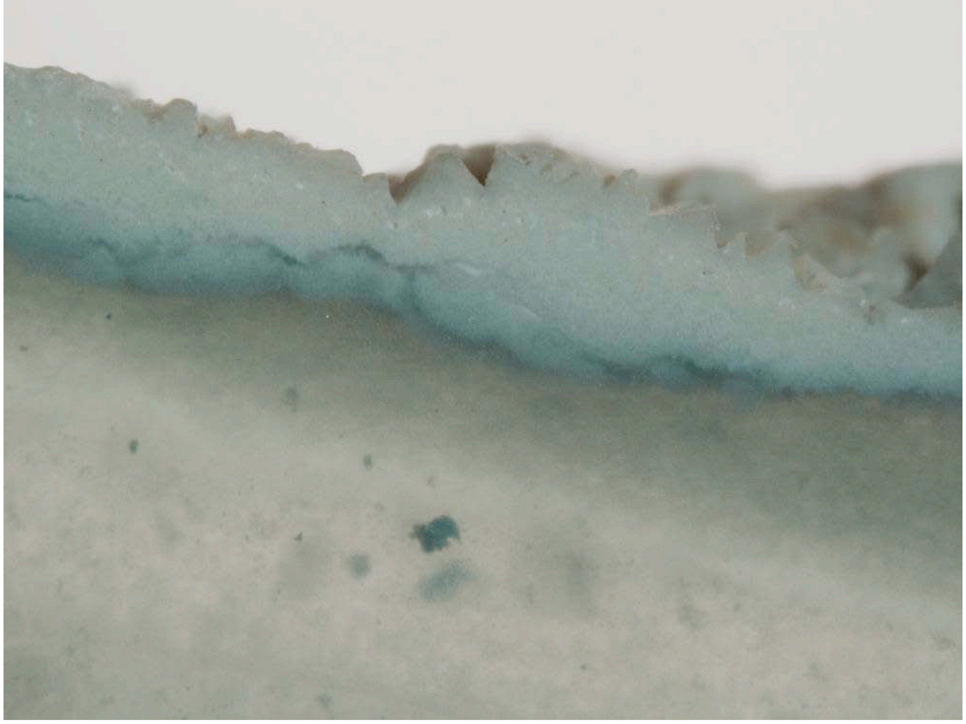

Figure 2. This close-up view shows some concentration of colors and color bands.

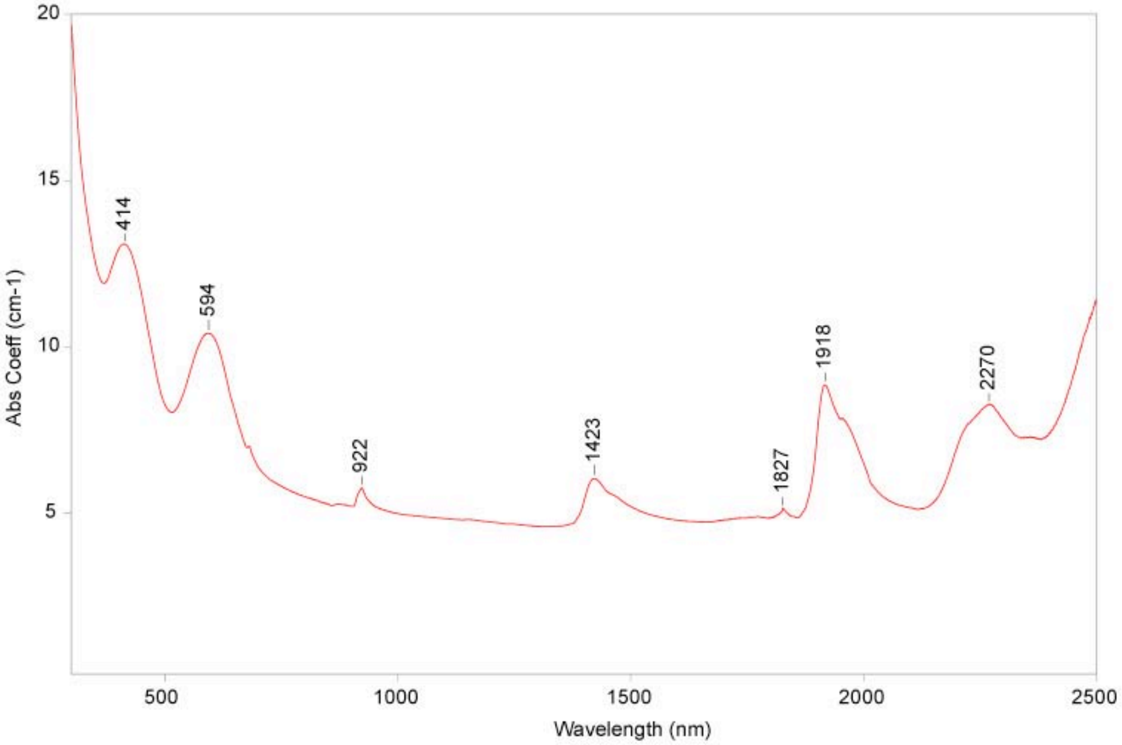

Figure 3. A UV-Vis-IR spectrum taken from the sliced sample shows the Cr^{3+} bands in the visible range and hydroxyl-related bands in the infrared region.

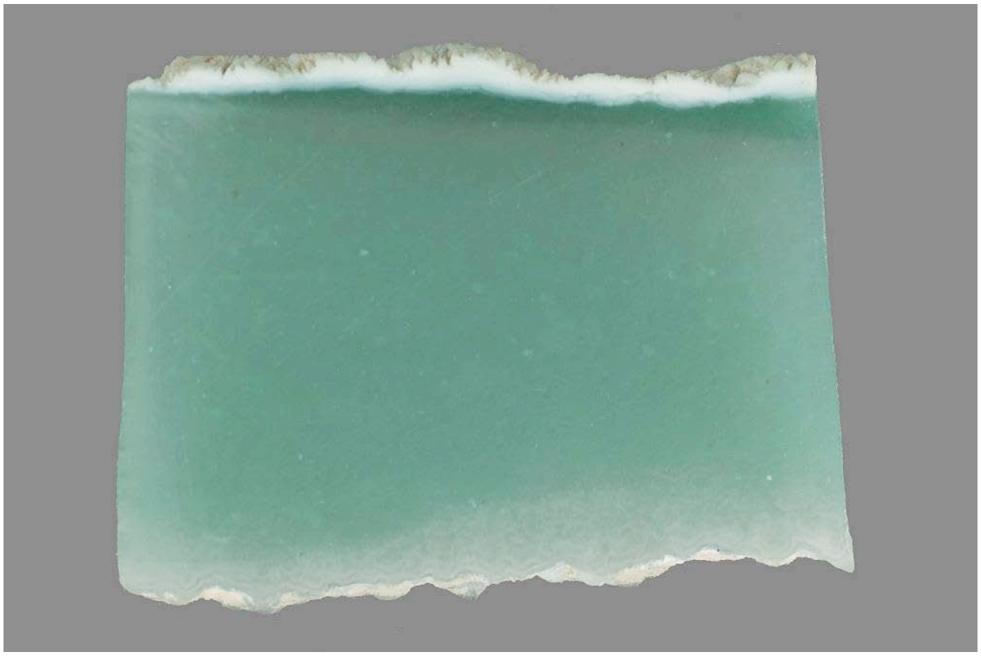

Figure 4. This slice (20 × 16 × 1.5 mm) was cut from the rough specimen.

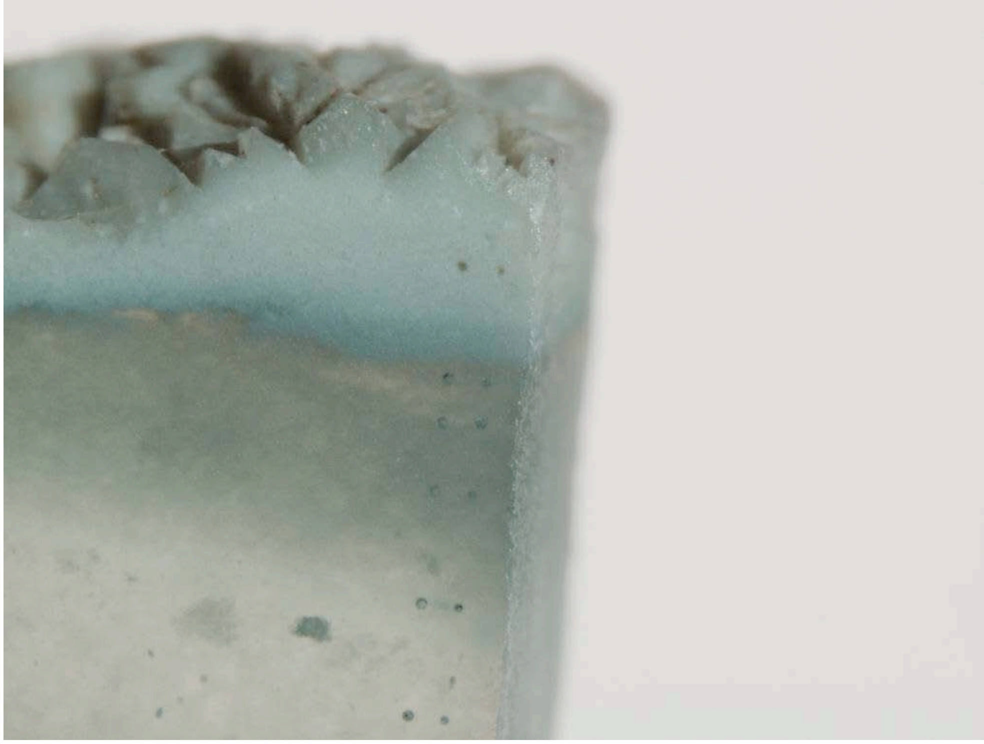

Figure 5. A close-up of the top right corner of the slab in figure 4 shows two vertical columns of LA-ICP-MS analysis spots. The 40 µm spots were in the right column and the 55 µm spots in the left column.

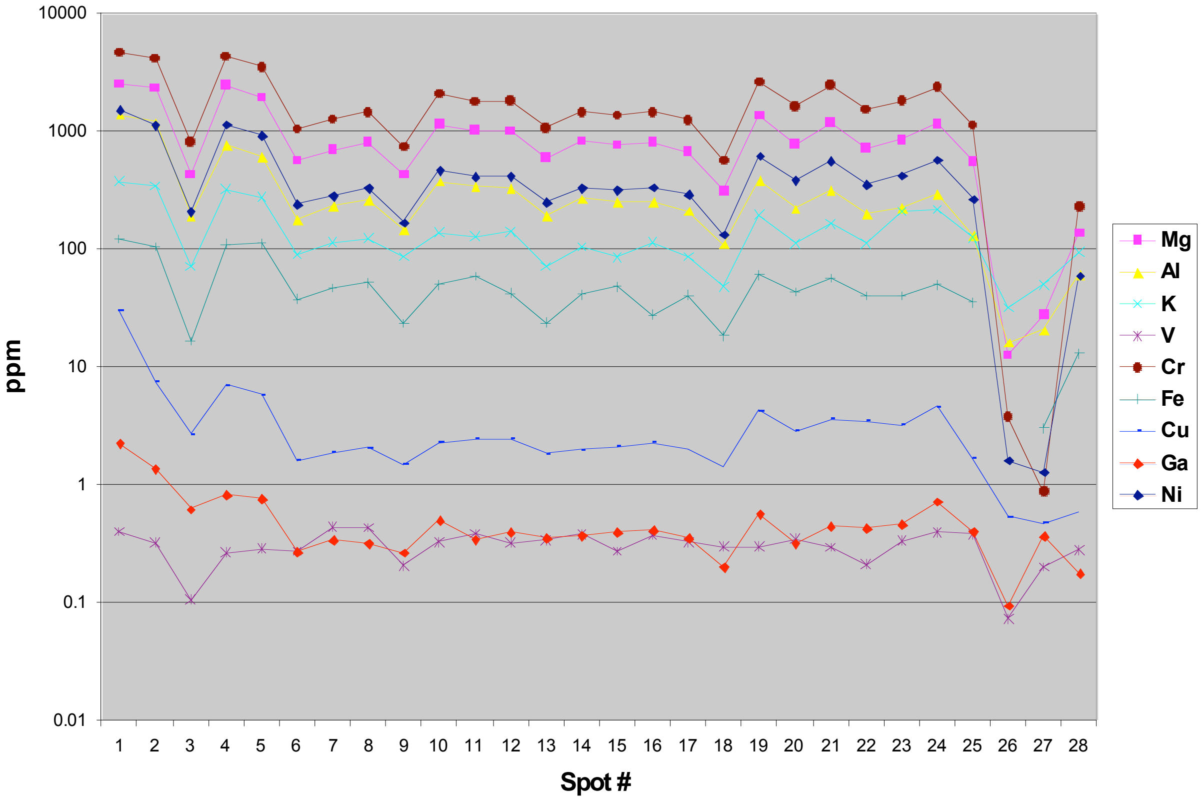

Figure 6. This plot shows variation of nine selected trace elements across the sample. A highly correlated trace-element pattern indicates natural trace-element distribution. (Note that the vertical scale is logarithmic.)