Using LA-ICP-MS Analysis for the Separation of Natural and Synthetic Amethyst and Citrine

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Quartz (SiO_2) occurs naturally in several color-based varieties. The most common varieties used in jewelry are amethyst (purple) and citrine (yellow). Rock crystal quartz (colorless) is also commonly carved or faceted. Of course, all natural colors of quartz can easily be synthesized in a laboratory by adding the appropriate color-producing elements to a growth chamber (figure 1). For a gemologist, though, the separation of natural from synthetic quartz is often no easy task. Similar hydrothermal growth processes in nature and the laboratory result in visually and structurally similar quartz samples. While natural and synthetic quartz have distinctly different crystal shapes, after faceting they can be nearly indistinguishable due to the high clarity and lack of inclusion features in most faceted quartz.

Figure 1. Natural amethyst and citrine (stone grouping on the right) and their synthetic equivalents (stone grouping on the left) exhibit similar color ranges. Photo by Don Mengason, GIA.

In an effort to provide additional scientific criteria for the separation of natural from synthetic quartz, we performed laser ablation–inductively coupled plasma–mass spectroscopy (LA-ICP-MS) trace element analysis on 52 natural and 65 synthetic quartz samples of various colors, rough and faceted (see table 1 for sample distribution). This study was intended to be an exploratory investigation of the value of chemical analysis in identifying quartz. These are preliminary results, and the investigation is ongoing.

Table 1. Sample distribution of natural and synthetic amethyst and citrine varieties.

Natural quartz						
Variety/color	Amethyst	Citrine	Colorless			
No. of samples	38	10	4			
Synthetic quartz						
Variety/color	amethyst	citrine	colorless	blue	green	pink
No. of samples	21	30	1	7	5	1

Gemological Tests

Gemologists have developed a few tests to facilitate the natural vs. synthetic quartz identification of faceted samples, but in many cases these tests are inconclusive and result in lab reports with "undetermined" comments. The gemological tests are focused on four properties: inclusion features, twinning, color zoning, and infrared absorption bands. Many quartz samples are very clean with few inclusions, but when natural crystal inclusions do occur, the identification is straightforward. Similarly, "breadcrumb" or other diagnostic synthetic inclusions are sometimes present (Gübelin and Koivula, 1986). The presence of Brazil-law twinning is one of the more reliable indicators of natural quartz (Crowningshield et al., 1986). This type of twinning occurs in most amethyst and some citrine and can be seen using a combination of immersion and either crossed polarized microscopy or a polariscope. Although this twinning can occur in synthetic amethyst (Koivula and Fritsch, 1989), it usually has a very different appearance. Color zoning can also provide some help with identification. In most natural amethyst and citrine, color concentrations occur along particular crystallographic directions, whereas many synthetics have even color distributions or an easily identifiable seed plate (Crowningshield et al., 1986). Infrared absorption spectroscopy has proven somewhat useful. A few absorption bands have been shown to occur primarily in natural amethyst, as reported in Zecchini and Smaali (1999).

Results of LA-ICP-MS Analysis

LA-ICP-MS analysis revealed several interesting trends in the chemical composition of natural and synthetic quartz, particularly for amethyst and citrine. An initial review of the data revealed that colorless rock crystal samples contained no elements other than Si in concentrations above the instrument detection limits (these limits varied for different elements, but were less than 0.5 ppm in most cases). In fact, even colorless zones within amethyst and citrine samples showed a similar lack of chemical composition. As a result, it was necessary to focus the chemical evaluation on analysis spots that were collected from colored zones. For both amethyst and citrine, these zones were readily identifiable by the presence of Fe, even when the color was not obviously visible.

While most element concentrations were below detection limits (BDL; we analyzed for ~72 elements) in all the samples, a few showed interesting results. In both amethyst and citrine samples, Ga proved to be very reliable for separating natural and synthetic quartz (figure 2). Natural amethyst and citrine showed Ga concentrations of 0.3–19.0 ppm and 0.7–10.0 ppm, respectively, whereas their synthetic counterparts showed little to no Ga content (BDL–0.2 ppm for both synthetic varieties). Although Ga enrichment in natural quartz was the most consistent and reliable distinguishing element, slightly elevated concentrations of Ti and Cr were also observed in many of the lab-grown samples. There was considerable overlap in plots of these two elements, but a much higher percentage of synthetic amethyst and citrine samples contained Ti and Cr than did the natural quartz stones (figure 2).

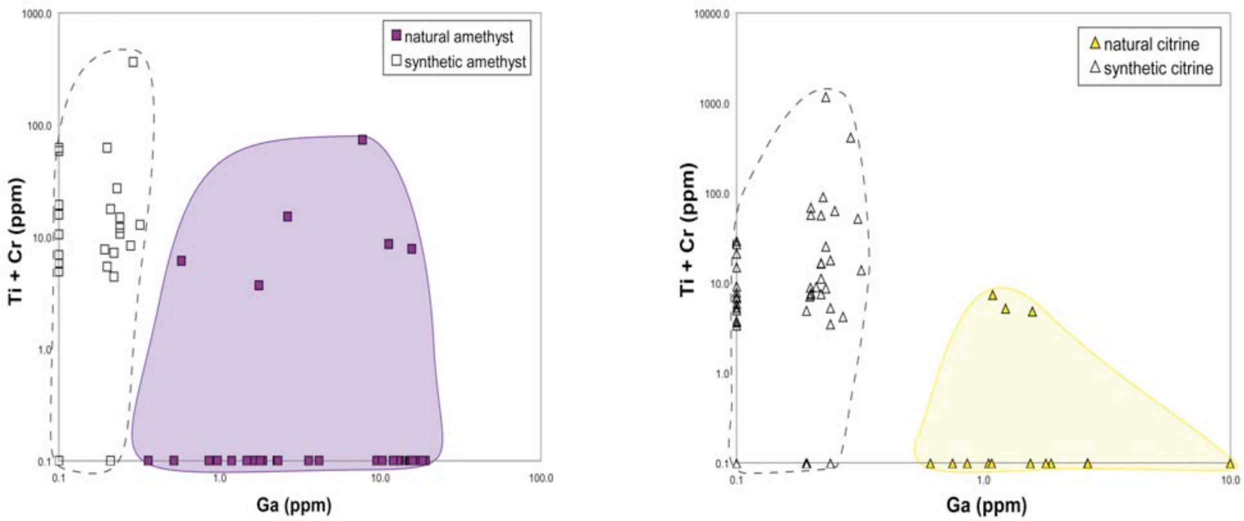

Figure 2. Chemistry plots for amethyst and citrine showing elevated Ga in natural stones and some Ti + Cr enrichment in synthetic samples. Note that the axes are log scale. (0.1 ppm was added to all plotted concentrations to facilitate log plotting of BDL results. Thus, a data point at 0.1 ppm represents a BDL result.)

Another trend observed in the amethyst samples was a weak correlation between Ga content and the geographic locality from which the samples were collected. The country of origin was known for 34 of the natural amethyst samples used in the study, including samples from Brazil, Uruguay, Namibia, Mexico, Canada, Zambia, Bolivia, Tanzania, and the United States. All amethyst samples from Zambia and Mexico showed Ga concentrations higher than 9 ppm, whereas those from Bolivia and Uruguay contained less than 1 ppm. Stones from the other countries contained approximately 1–8 ppm Ga. While this is interesting data, many more samples must be analyzed to evaluate how reliable Ga might be for determining the geographic origin of amethyst.

Preliminary Conclusions

LA-ICP-MS analysis of some varieties of quartz can be a reliable tool for distinguishing natural and synthetic samples. While colorless quartz cannot be evaluated by this method due to its relatively pure composition, preliminary data from natural amethyst and citrine samples showed elevated concentrations of Ga that appear to be useful for separation from lab-grown equivalents, which show little to no Ga content. In addition, Ga content appears to be potentially helpful in determining the geographic origin of some natural amethyst. Cr and Ti contents may also be useful in identifying synthetic quartz samples. Great care must be taken, however, to analyze zones that show color (rather than colorless regions). The presence of Fe is helpful in confirming that colored growth zones have been sampled. Further refinement of LA-ICP-MS analysis is the subject of ongoing research at GIA.

References

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