ARTIFICIALLY INDUCED COLOR IN AMETHYST-CITRINE QUARTZ

By Kurt Nassau

Adjacent amethyst and citrine colors in the same crystal of quartz have been reported from South America, although there appears to be uncertainty as to the exact locality of origin. Such material has also been produced by synthesis. Several previous studies on the impurities contained in natural and synthetic quartz and the effects of irradiation and heating, as well as new heating and irradiation experiments with the current natural amethyst-citrine quartz and with amethyst, are described. It is concluded that there are presently no known tests to distinguish natural bicolor material that was heated or irradiated (or both) in nature from natural amethyst heated or irradiated (or both) by man or from the equivalent synthetic material.

Figure 1. Natural amethyst-citrine quartz, 108.5 carats (from the Los Angeles County Museum of Natural History collection).

A new and rather unusual gem material has been reported recently, namely, the occurrence of citrine and amethyst colors side by side in the same crystal of quartz. Brief descriptions have been given by Hehar (1980), Koivula (1980), and Vargas and Vargas (1980). The locality was originally reported as being in the Rio Grande do Sul mining area of Brazil, close to the Uruguay border, or in northern Uruguay itself; subsequently it has been reported to be in Bolivia (G. Vargas and J. Koivula, personal communications). The names *amethyst-citrine quartz, citrine-amethyst quartz, ametrine, trystine,* and *golden amethyst* have been used for this material. The first of these is a clear and descriptive designation and will be used below. The well-cut stone shown in figure 1 clearly displays both colors.

Usually, a gemstone material is synthesized after naturally occurring material provides the stimulus for duplication attempts. In this instance, however, the author has had a piece of *synthetic amethyst-citrine quartz* in his possession for several years without realizing its significance! This unusual specimen is shown in figure 2, where the purple amethyst and yellow citrine colors can be clearly seen.

A general description of the growth of synthetic quartz has been given by the author (Nassau, 1980a and 1980b). The causes of color in quartz have been reviewed by Nassau and Prescott (1977). Briefly, citrine and amethyst are caused by the incorporation into quartz of different types of iron; amethyst also involves irradiation. The amounts of the two types of iron present in a quartz crystal depend on the growth direction and on other growth factors, but either type may be present by itself or they may both be present in variable ratios. It has long been known that the depths of the colors do not correlate with the analyzed iron concentration; this is a result of the presence of a third type of iron, which is not color producing.

Many scientific studies have also been conducted over the years on the impurities contained in natural and synthetic quartz, together with the effects of irradiation and heating (Cox, 1977;

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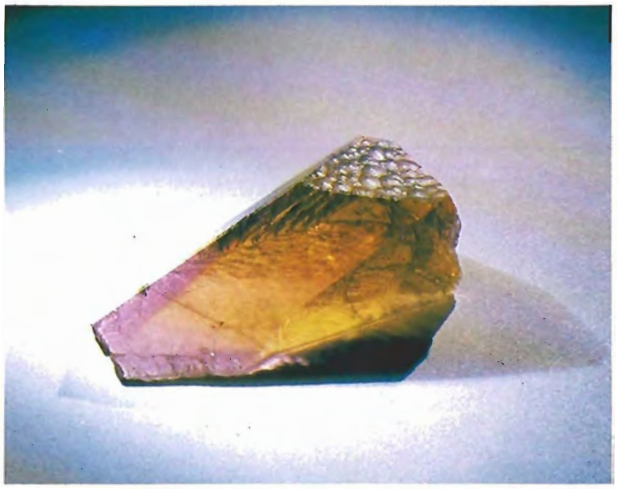

Figure 2. Synthetic amethyst-citrine quartz crystal, 3 cm long (author's collection).

Cohen and Hassan, 1974; Hassan, 1972; Cohen, 1975; Lehmann, 1975; and Nassau and Prescott, 1977 and 1978). These studies, as well as some current experiments, suggest that several possibilities exist as to the origin of any specific piece of amethyst-citrine quartz.

NATURAL AMETHYST-CITRINE QUARTZ

In their reports, Hehar (1980), Vargas and Vargas (1980), and Koivula (1980) note six alternating regions, three each of amethyst and citrine, which clearly correspond to the major-rhombohedron growth regions of typical amethyst and the minor-rhombohedron growth regions of typical citrine. There are three significantly different ways in which such naturally occurring amethyst-citrine quartz could have been formed. First, it is possible that the quartz simply grew under such conditions that the amethyst-forming iron was incorporated under the major-rhombohedron faces, while only citrine-forming iron entered under the minor-rhombohedron faces (some may, of course, be present under the majors as well). Natural irradiation would then produce this end product.

There are, however, important alternative possibilities involving different mechanisms. In the second suggested mechanism, both amethyst-producing iron and citrine-producing iron are present in all sectors of the quartz, and the naturally occurring irradiation has produced an amethyst color in all sectors. According to the second scheme, the quartz next would have passed through a heating stage that bleached the minor-rhombohedron amethyst to leave citrine, but which did not bleach the major-rhombohedron amethyst material. According to the third scheme, heating could have affected the material in such a way that a subsequent irradiation might have colored only some parts, thus producing the observed end product.

According to these alternative schemes, the important difference is not in the quantities of iron occupying the different sites, (although some such differences may be present), but in the behavior of the material with respect to heating. The determining factor is either the temperature at which the amethysts bleach (i.e., at which the color centers are destroyed) or the temperature of heat treatment after which the citrine can no longer be converted to amethyst. Such differences (e.g., in the bleaching temperatures) do occur in quartz (Nassau and Prescott, 1977), and sectored variation in properties has also been noted in conjunction with the pleochroic anisotropy in smoky quartz color centers (Nassau and Prescott, 1978) and in amethyst (Cox, 1977). There are two questions that arise should one of these schemes apply: (1) Was the heating or irradiation (or both) a naturally occurring event or was it performed by man? and (2) Is this property unique to the locality or will amethyst from other localities produce the same result if suitably treated?

HEATING AND IRRADIATION EXPERIMENTS

Specimens of the natural amethyst-citrine currently in the trade were made available to the author by the very kind cooperation of G. Vargas and by J. I. Koivula and D. V. Manson of the GIA.

Parts of two specimens were irradiated in a cobalt-60 gamma-ray cell to a dose of at least 1,000,000 rads. As a result, portions of some of the amethyst and citrine regions acquired an additional weak smoky tint. Heating to 350°C removed this tint and restored the specimens to their original state.

Parts of two different specimens were next heated in air in a furnace for two-hour periods first at 250°C and then at successively higher temperatures at intervals of 50°C. The amethyst sectors became yellow after the two hours at the 400°C step; the citrine regions were not affected by this heat treatment. A subsequent irradiation followed by heating to 350°C to remove smokiness restored the original amethyst-citrine colors.

In order to obtain comparison data, experiments were also performed on two specimens of sectored amethyst from Minas Gerais, Brazil, which were also obtained from the Gemological Institute of America. These specimens exhibited alternating sectors of dark (major rhombohedron) and pale (minor rhombohedron) amethyst. Duplication of the first irradiation experiment above gave essentially the same results: smoky purple and pale smoky purple, with the smoky component removed and the original state restored upon heating to 350°C.

Heating the sectored amethyst to successively higher temperatures, however, produced an unexpected result: the dark purple sectors became somewhat lighter but the pale purple sectors turned yellow at 400°C. To the eye, this material now had exactly the same appearance as the amethyst-citrine. Subsequent irradiation and heating to 350°C restored the original all-amethyst state. This process corresponds to the second mechanism discussed above, but the end product is unlike the current amethyst-citrine, which did not convert to all-amethyst even after 20 megarads of cobalt-60 gamma rays.

Heating of these same sectored-amethyst sections to the slightly higher temperature of 450°C bleached all the amethyst sectors to yellow. A subsequent irradiation followed by heating to 350°C reproduced not only the appearance of the current amethyst-citrine, but also its behavior with respect to heating and irradiation: it could no longer be returned to all-amethyst. A specimen of this treatment-produced amethyst-citrine (see figure 3) has been returned to the Gemological Institute of America for archival purposes.

Iron analyses were not performed because such analyses cannot distinguish among the three types of iron but only give the total iron present; this total has not provided useful information in previous studies.

DISCUSSION

The above experiments show that the amethyst-citrine combination in quartz can be obtained by heat-treating sectored amethyst from Minas Gerais, Brazil, in either one of two ways: (1) a medium heating step produces the change, but this can be reversed by irradiation; (2) a more intense heating followed by irradiation and a second, gentle heating also produces the change, but the product can no longer be returned to all-amethyst.

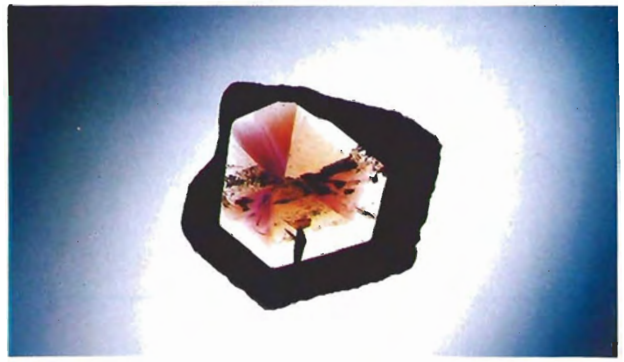

Figure 3. Amethyst-citrine quartz produced by heating and irradiating sectored amethyst from Brazil; 12 mm across.

Since the sectored amethysts tested were merely randomly chosen, it is likely that much such material from a variety of sources can be treated to produce amethyst-citrine, including man-made quartz. There are no known tests to distinguish the origin of color of natural material that was heated/irradiated in nature from natural amethyst heated/irradiated by man or from the equivalent synthetic material.

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