AMETHYST ON MILKY QUARTZ FROM HOPKINTON, RHODE ISLAND

John Rakovan
Department of Earth and Space Sciences
State University of New York
Stony Brook, New York 11794-2100

David B. Mitchell and Laurie D. Benton
Department of Geosciences
University of Tulsa
600 S. College Avenue
Tulsa, Oklahoma 74104

Sal Avella
7 Homestead Avenue
Smithfield, Rhode Island 02917

The eastern United States is well-known for its many occurrences of exceptionally well-formed amethyst specimens. In the spring of 1981, an occurrence of amethyst scepter overgrowths on milky quartz was discovered in Ashaway Village, Hopkinton, Rhode Island. This deposit has produced some of the most beautiful amethyst specimens found in the Piedmont of the eastern United States.

INTRODUCTION
The recovery of sceptered amethyst on Diamond Hill, Ashaway Village, Hopkinton, Rhode Island has been described by Metropolis et al. (1986). These specimens were collected from subsurface quartz veins after removal of 1 to 3 meters of overburden. To date, a total area of approximately 6 x 9 meters has been excavated to a depth of 3 to 4 meters. In the latest excavation, August 1991, approximately 80% of the area so far uncovered was searched, yielding only eight noteworthy mineral specimens. Altogether approximately 500 to 600 single crystals (scepters) and 35 crystal groups with amethyst have been collected from the site since 1981. Some of the finest specimens recovered are in the collections of the National Museum of Natural History in Washington, the American Museum of Natural History in New York, and the Harvard Mineralogical Museum in Cambridge. The site is on private property and collecting is currently prohibited by the owners.

The formation of epitaxial amethyst overgrowths on euhedral milky quartz stems results from distinct changes in the physiochemistry of the fluids from which the quartz precipitated. Physiochemical data suggest a hiatus between the formation of the two quartz types. In this study, fluid inclusion and stable isotope geochemistry are used to constrain the mode of formation of the quartz.
Ramsey (Universitat Bern, Switzerland) using the instrumentation and methods detailed by Ramsey et al. (1988, 1989). The CL technique enables the identification of different generations of growth within a single crystal. CL analysis was conducted on two amethyst overgrowths with milky octahedral bases cut parallel to the c-axis and one milky stem cut perpendicular to the c-axis.

Primary, aqueous liquid-vapor (L-V) inclusions (criteria of Roedder, 1984) were observed in both the amethyst overgrowths and the milky quartz. The temperature range ($T_{li}$), and salinity of the fluids present when the quartz precipitated were determined from analysis of these aqueous (L-V) inclusions.

$T_{li}$ can be used to find the minimum possible temperatures of fluid inclusion entrapment, but a pressure correction may be required to equate $T_{li}$ to the true temperature of trapping ($T_p$).

Waters from fluid inclusions were analyzed for hydrogen isotopic ratios, and the quartz was tested for oxygen isotopic ratios. Stable isotopes are reported as delta ($\delta$) values, defined as $\delta(X) = (R_s - R_{std} / R_{std}) \times 10^3$, where $R_s$ is the isotopic ratio of the sample (e.g. D/H or $^{18}$O/$^{16}$O) and $R_{std}$ is the isotopic ratio of a standard. $\delta^{18}$O values were obtained from bulk samples of separated amethyst overgrowths and milky quartz stems.

RESULTS

Quartz Mineralization

Three varieties and several different habits of quartz crystals are present. Optically transparent quartz occurs as elongated, pencil-like euhedral crystals with a length-to-width ratio of 6:1 or greater. These commonly occur in tightly packed groups of crystals in parallel growth. The transparent quartz also occurs as short prismatic crystals that commonly are flattened perpendicular to (1010). Frequently these crystals have one well-developed (1121) face.

Euhedral milky quartz is the most abundant variety found. The crystals are typically uniform and prismatic with development of (1010), (1011) and (1011) only. These crystals have a transparent core and a thinner concentric rim of alternating transparent and milky layers. The opaque, milky layers result from an increased concentration of microscopic fluid inclusions in the quartz. Rhombohedral faces are smooth whereas prismatic faces are covered by a layer of small crystals in parallel growth, leading to a macroscopically rough surface.

Amethyst is the third variety of quartz that occurs at this site. In almost all cases the amethyst occurs as “scepters” or epizonal overgrowths on milky quartz crystals. These overgrowths are equant in habit, with the base of the amethyst overgrowth terminated and forming a re-entrant with the euhedral stem. This overgrowth produces a scepter with a mushroom-like appearance. The re-entrant always starts where the amethyst overgrowth comes in contact with the rough prism faces of the milky quartz. This suggests that the habit of the amethyst overgrowth is partially controlled by the surface topography of the milky quartz stems. Amethyst is found sparsely throughout the veins, and groups or plates of milky quartz crystals tend to have very few scepters. The largest group of scepters found contains 23 amethyst caps on a 25.4 x 30.5-cm plate of milky crystals. Several specimens exhibit amethyst that has grown in a random fashion on the fracture surfaces of brecciated blocks of vein quartz. These are all elongated in habit, rather than equant; this further indicates the role of the milky
GEOLGY

Basement exposures in southwestern Rhode Island are dominated by multiply deformed late Proterozoic to late Paleozoic plutonic and metasedimentary rocks (Fig. 1). Many of the granite intrusions are of Permian Westerly and Narragansett Pier granites. Medium-grained phaneritic and pegmatitic granite dikes, most likely associated with the Permian granitic suite, are locally abundant. Diamond Hill is formed on the western limb of a north-south-trending syncline with displacement along a major fault that cuts across the southwestern corner of Rhode Island (Feininger, 1965). The quartz lies stratigraphically above a lithologically variable quartzite unit of the Proterozoic Plainfield Formation (Feininger, 1965) and is, in turn, overlain by 0.6 to 1.6 meters of glacial till.

The amethyst specimens occur in two quartz veins, each approximately 36 cm thick. No surface exposure of these quartz veins has been found, and they have only been accessible where small temporary pits have been dug during excavation. Consequently, little field data regarding the relationship of the veins to the regional geology is available. The veins are composed of a mosaic of partially displaced quartz blocks and are embedded in a clay sequence that is encountered 2.5 to 4.6 meters below the ground surface (Fig. 2). The clay is not related to the overlying till. The veins are almost entirely quartz. Some small mica crystals have been found intermixed with quartz blocks and clay; however, these may have been introduced during excavation. A contact between the deposit and the underlying bedrock has not been encountered, although a band of small displaced blocks of Plainfield quartzite has been found intermixed with the clay. Amethyst crystals are interspersed with the clay and vein blocks, and no open mineralized pockets or vugs were found. The clay unit is composed primarily of illite, kaolinite and quartz as determined by X-ray powder diffraction.

ANALYTICAL TECHNIQUES

Cathodoluminescence (CL), stable isotopes, fluid inclusions and trace elements have been utilized in this study to analyze the quartz and fluid chemistry. Standard techniques were used in the analysis of stable isotopes and fluid inclusions. (Complete experimental details can be obtained from the author or from the Mineralogical Record editorial office.) Trace element abundances were determined quantitatively by synchrotron X-ray fluorescence microanalysis (SXRFMA). For a detailed description of trace element analysis in minerals by SXRFMA see Rakovan and Keeler (1994).

CL analysis of amethyst and milky quartz was performed by D. K.
Figure 3. Single amethyst scepter on a group of Hopkinton milky quartz crystals 8.9 cm across. Russell Behnke specimen.

Figure 4. Amethyst on milky quartz from Hopkinton. The specimen measures 12.7 x 15.2 cm. John Travasso specimen; photo by John Rakovan.

Figure 5. Amethyst on milky quartz from Hopkinton. The specimen measures 12.7 x 25.5 x 30.5 cm, and the largest scepter is 2.5 cm across. Sal Avella specimen; photo by John Rakovan.
quartz substrate in influencing the habit of the amethyst when epitaxially related.

Most of the scepters are 3 to 12 cm long in the c direction, but a single exceptional scepter measures 20.3 cm in length. Amethyst overgrowths range from about one-half to twice the width of the milky quartz stems. The amethyst is usually fairly transparent, with color ranging from faint violet to a deep purple. The amethyst is commonly sector-zoned with respect to color. Here, the color centers (causing the purple color) are concentrated in rhombohedral sectors and depleted in the prismatic sectors. Thus, a central band perpendicular to the c-axis is visible as clear to faint violet color in the overgrowths. Even though most of the amethyst is strongly color-zoned, a few dozen exceptional stones have been cut for gems. The largest cut stone weighs approximately 45 cts and currently resides in the collection of Rhode Island Senator Claiborne Pell.

Electron probe microanalysis indicates that the quartz is stoichiometric with no Fe or other trace elements detectable within instrumental resolution. SXRFMA was used to determine trace element chemistry. SXRFMA detected only very small amounts of Fe and Ga in the amethyst, 1 to 10 ppm range. No detectable Fe was found in the milky quartz.

Cathodoluminescence
CL reveals concentric zoning in the milky quartz. Several different
generations of growth are distinguishable on the basis of variations in blue luminescence. There is a central zone of quartz that correlates with the previously discussed transparent core that lacks fluid inclusions. A second generation of quartz is delineated by large primary fluid inclusions. There is also a third generation of quartz with few fluid inclusions. A fourth generation of quartz growth also displays a high density of fluid inclusions. A highly zoned transitional phase of quartz concludes the growth of the milky stems. The amethyst overgrowths exhibit very dull luminescence. Limited areas of the basal terminations of the amethyst overgrowths show deep blue luminescence.

Fluid Inclusions

Microscopically, the contact between the amethyst overgrowth and the milky quartz is indistinguishable but for the presence of fluid inclusions. In the milky quartz the abundance of fluid inclusions is very high. Individual fluid inclusions are commonly over 100 μm in greatest dimension, but throughout the size range, the liquid/vapor ratio is consistent. This consistency of the liquid/vapor ratio may reflect uniform conditions of entrapment of the fluid in the milky quartz. Conversely, the amethyst overgrowths contain very few fluid inclusions. Those present have maximum dimensions between 5 and 10 μm.

The calculated salinities for the fluid inclusions in the amethyst are from 0.2 to 15.7 eq. wt. % NaCl (mean value 7.8), with these data displaying significant scatter. For the milky quartz they range from 7.7 to 15.8 eq. wt. % NaCl (mean value 14.7). No daughter crystals were observed in either type of quartz. Density ranges from 0.9227 to 1.0574 g/cm³ (mean value 0.9972) for the amethyst and 0.9695 to 1.0427 g/cm³ (mean value 1.0199) for the milky quartz.

Tₜₐ ranges from 94.5 to 140.7 °C (mean value 124.6 °C) for the fluid inclusions in the amethyst overgrowths. For the fluid inclusions in the milky quartz, however, the Tₜₐ is different, ranging from 125.5 to 186.9 °C (mean value 156.4 °C).

![Figure 10. δD-δ¹⁸O plot showing isotopic compositions and fields of Hopkinton quartz fluid inclusions, primary magmatic waters, metamorphic waters, and standard mean ocean water (SMOW). The line across the upper left part of the graph is the compositional line for meteoric waters.](image)

Stable Isotopes

Oxygen isotope ratios were determined for the milky quartz and amethyst overgrowths. These values were calculated to represent δ¹⁸O using the appropriate equation from Clayton et al. (1972). The values range from -3.5 to -2.2 ± 0.2 % for the milky quartz and from -6.0 to -3.1 ± 0.2 % for the amethyst overgrowths. The δD values for the inclusion waters from the milky quartz range from -8.7 to -6.3 ± 2.0 % (SMOW). Because of the low abundance of fluid inclusions in the amethyst overgrowths, the amount of water obtained from the inclusions by thermal decrепiation was less than ideal. As a result, only one δD value of -42 ± 4.0 % (SMOW) was obtained for the amethyst overgrowths.

DISCUSSION

The poor exposure of this deposit has made interpretation of its mode of formation difficult. Initially, Metropolis et al. (1986) postulated that the quartz veins and surrounding clay were the product of intense weathering of a prograding granitic dike or sill. Quartz precipitated from a granitic source will have a geochemical signature indicating such a source. For example, primary fluid inclusions in the quartz represent the fluids from which the crystals formed. One tool in the determination of the origin of these waters is to use the variation in the isotopic ratios of oxygen and hydrogen. The δ¹⁸O and δD values can help constrain both the source and history of a water (Valley et al., 1986).

When the δD values are plotted versus the δ¹⁸O values for the amethyst and the milky quartz, both boxes of data plot close to the meteoric water line (Fig. 10). The meteoric water line represents water that is derived from atmospheric precipitation. This implies a relatively shallow depth of quartz formation, such that the water had insufficient time to interact with waters from other sources. In Figure 10 the separation of the δD and δ¹⁸O for the amethyst and milky quartz along the meteoric water line suggests that a differently sourced meteoric water was present during formation of each quartz type. Such a shift could be the result of a temporal difference between the precipitation of the two quartz types and may also reflect a temperature difference during growth. An interesting feature in Figure 10 is the shift in δ¹⁸O of the amethyst from the meteoric water line towards higher values. Such an oxygen-isotopic shift is a common feature in geothermal waters and has been interpreted to be from the interaction of meteoric waters with country rock at elevated temperatures (Hoefs, 1980).

Salinities of fluid inclusions in both the amethyst and milky quartz are comparatively low with respect to igneous or metamorphic waters. Fluids from the milky quartz are slightly more saline than those of the amethyst. Waters from igneous sources commonly become supersaturated with respect to NaCl, resulting in the formation of daughter crystals in inclusions.

The temperatures of homogenization for the primary fluid inclu-
sions in the two types if quartz are in the range of 90 to 180 °C; this is below the temperatures expected for igneous environments. These $T_{\text{eq}}$ values represent the minimum possible temperatures of fluid inclusion entrapment. A correction for pressure is required to equate $T_{\text{eq}}$ to the true temperature of trapping. No independent pressure data are available. However, based on the meteoric signature of the fluid inclusions, the low salinities of the fluid inclusions, and the low level of detectable trace elements in both the quartz and fluid inclusions, we postulate that the $T_{\text{eq}}$'s are close to the true temperature of entrapment and that precipitation occurred close to the earth's surface. Furthermore, the almost complete lack of minerals other than quartz, kaolinite and illite suggests primary deposition as opposed to weathering of pre-existing minerals. Based on all of the above data, the quartz shows fewer or no features of igneous formation. Rather, the data suggest that precipitation occurred from epithermal meteoric waters along conduits in the adjacent Plainfield quartzite.

CL variability is related to variations in luminescence-activating trace element concentration. Concentric zoning in the milky quartz is seen as differences in fluid inclusion density and in CL. The concentric zoning indicates fluctuations in physical and chemical parameters (e.g., temperature, pressure, composition of the fluid or pH) in the environment during growth.

Differences in color, CL, and fluid inclusion characteristics (salinity, $T_{\text{eq}}$, and isotopic ratios) indicate either continuous growth accompanied by significant changes in the environment, or a hiatus between the precipitation of the milky quartz and amethyst. Several specimens contain amethyst that have not grown epitaxially on the terminations of milky quartz crystals but are attached to fracture surfaces of brecciated blocks of vein. This amethyst is identical to the amethyst caps in every manner other than habit. Such specimens suggest that there was a hiatus between the formation of the two types of quartz, during which time the milky quartz veins were brecciated.

For the well-formed euhedral crystals of milky quartz and amethyst to form they most likely grew into open spaces in the veins. No cavities have been found, suggesting collapse at some point of pre-existing pockets. Excavation of the site revealed that the majority of amethyst occurs in a very localized area (approximately 1 x 2 meters). Of the 12 individual pits that have been dug only a few exposed more than a handful of specimens. The localization, absence of open pockets, brecciation of the quartz veins, and the presence of displaced blocks of the Plainfield quartzite intermixed with the clay suggest that the deposit has moved, possibly by the action of surface slumping or glaciation.

Contrary to initial speculations, the geochemical evidence demonstrates that the quartz is not related to an igneous source, but rather has precipitated from meteoric waters during several stages of precipitation.

The sceptered amethyst specimens from Hopkinton are undoubtedly some of the finest examples found in the eastern United States (see White and Cook, 1990), and are arguably some of the finest mineral specimens to be recovered in the state of Rhode Island. Recent excavations have resulted in very few additional specimens, however, and the future potential of the site is uncertain.

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REFERENCES


