

## Fibrous nanoinclusions in massive rose quartz: The origin of rose coloration

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### ABSTRACT

Pink nanofibers were extracted from rose quartz from 29 different pegmatitic and massive vein localities throughout the world. Their width varied from 0.1 to 0.5  $\mu\text{m}$ . On the basis of optical absorption spectra of the fibers and the initial rose quartz, we conclude that these nanofibrous inclusions are the cause of coloration of massive rose quartz worldwide. These fibers do not occur in the rare, euhedral variety of pink quartz. Redox and heating experiments showed that the pink color of the fibers is due to Fe-Ti intervalence charge transfer that produces an optical absorption band at 500 nm. Based on the XRD patterns and characteristics of pleochroism, the best match for these inclusions is dumortierite. However, FTIR and Raman spectra consistently did not exactly match the standard dumortierite patterns, suggesting that this fibrous nano-phase may not be dumortierite itself, but rather a closely related material.

### INTRODUCTION

The rose variety of quartz is known and valued from time immemorial as an item of beauty, a source of rock for decorative carvings, and as a jewelry stone. Even though it is one of the less common colored varieties of quartz, rose quartz is found at numerous localities around the world.

Massive rose quartz occurs most commonly in granitic pegmatites and sometimes in massive hydrothermal veins. It makes up the whole or part of the core and/or joins together the potassium feldspars of the blocky zones of pegmatites (Cassedanne and Roditi 1991). Associated minerals are schorl, cassiterite, beryl, and phosphate minerals. Coloration of massive rose quartz varies from bright to pale pink, sometimes with lavender or orange overtones. It is always slightly to highly turbid.

In spite of extensive studies over the last century, the source of the rose coloration in quartz still remains a subject of active debate. Many possible mechanisms for the color of rose quartz have been proposed (reviewed in Rossman 1994), but no consensus has developed. The proposed causes of pink color in quartz can be divided into three groups: (1) the presence of individual substitutional or interstitial ions in the quartz structure; (2) charge transfer between pairs of various transition elements in the quartz structure; or (3) the presence of mineral inclusions.

Based on chemical analyses, Holden (1924a, 1924b) argued that rose color in quartz is due to  $\text{Mn}^{3+}$  pigmentation. In contrast, many researchers later attributed the color to the presence of  $\text{Ti}^{3+}$  (Wright et al. 1963; Lehmann 1969; Cohen and Makar 1984).

Other workers have suggested that the color of rose quartz is due to intervalence charge transfer (IVCT) between  $\text{Fe}^{2+} + \text{Ti}^{4+} \rightarrow \text{Fe}^{3+} + \text{Ti}^{3+}$  (Smith et al. 1978) or between substitutional  $\text{Ti}^{4+}$  and interstitial  $\text{Ti}^{3+}$  (Cohen and Makar 1985).

Turbidity and scattering of light in massive rose quartz suggests the presence of a second mineral phase. Fine, submicrometer diameter oriented needles were observed and identified as rutile by many workers (e.g., Holden 1924a; Gordon 1945; Wright et al. 1963; Lehmann 1969). Vultee (1955) and Vultee and Lietz (1956) argued that scattering of light by rutile is the real cause of the rose color. Later work by Dennen and Puckett (1971) supported this argument and concluded that the color of rose quartz results from Tyndall scattering by tiny oriented rutile needles. Other pink phases such as tourmaline and manganiferous clays have been identified as inclusions in pegmatitic quartz, but their relationship to common, massive rose quartz has not been explored.

More recent studies presented different inclusions in rose quartz as an alternative to rutile. By HF etching of metaquartzite, Folk (1989) noticed fibrous resistant inclusions in quartz, which he presumed to be aluminosilicates. Applin and Hicks (1987) found that pink microfibers included in massive rose quartz from Montana and South Dakota yielded an X-ray diffraction pattern compatible with that obtained for dumortierite,  $\text{Si}_3\text{B}[\text{Al}_{6.75}\square_{0.25}\text{O}_{17.25}(\text{OH})_{0.75}]$  by Moore and Araki (1978). Ignatov et al. (1990) observed macroscopic (2–3 mm) as well as submicrometer size inclusions in a rose quartz specimen from a vein in a biotite-muscovite schist from the Caucasus Mountains. Fine inclusions were oriented perpendicular to the c-axis of the quartz crystal. Clusters of larger prismatic needles were identified as

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dumortierite. The authors extrapolate their phase identification to the submicron size inclusions and conclude that these two types of inclusions (oriented and clustered) represent two generations of the same mineral, dumortierite. Optical absorption spectra, taken from a ~2 mm cluster, are similar to the optical spectra of the rose quartz itself. This study and the work of Applin and Hicks (1987) motivated us to raise the question of a more global role of dumortierite or other mineral inclusions in rose quartz coloration.

A further complication comes from reports about the lack of photo- and thermo-stability of rose quartz. Cassedanne and Roditi (1991) report that in some Brazilian deposits, specimens on the surfaces of mine dumps turned milky white over a few years. Fading is often a characteristic of color centers from radiation damage. In other deposits, fragments dumped more than 50 years ago do not show any fading. There are reports that massive rose quartz is unstable under heat. Experiments by Ignatov et al. (1990) showed that the color of rose quartz is lost at ~500 °C. At this temperature, the larger, clustered inclusions in the quartz lost their color but did not change to another phase.

Although normally found in massive aggregates, rose quartz also occurs in a few pegmatites as euhedral crystals. Based on their optical properties and chemical composition, the coloration of these two types of rose quartz appears to be of a different nature. Massive quartz is slightly to highly turbid, indicating the presence of the second phase, whereas single-crystal rose quartz (sometimes called pink quartz) is nearly devoid of internal scattering when probed by a narrow laser beam. In addition, single-crystal rose quartz is photochemically unstable, and, unlike massive rose quartz, it is extremely rare.

EPR spectra of natural euhedral rose quartz showed that this

type of rose quartz contains hole centers induced by ionizing radiation. Maschmeyer and Lehmann (1983) have attributed rose quartz color to these centers. Their model consists of substitutional Al and P atoms bridged by O<sup>-</sup> ions. This is further substantiated by Balitsky et al. (1996) who synthesized single-crystal rose quartz that contains these types of centers. The Al-O-P centers are responsible for the photochemical instability. EPR studies of some synthetic euhedral rose quartz also revealed [SiO<sub>4</sub>/Li]<sup>0</sup> centers (Bailey and Well 1991) and [TiO<sub>4</sub>]<sup>-</sup>.

This work concentrates only on common massive rose quartz. By extraction of inclusions from pegmatitic and hydrothermal vein rose quartz from different localities, we explored whether there is a general relation between the presence of nanofibers and the origin of color in rose quartz. We tried to understand whether massive rose quartz commonly contains fibrous inclusions, whether nanofibers are the reason for its coloration, and what mineral phases make up those nanofibers.

## MATERIALS AND METHODS

### Sample preparation

The massive rose quartz samples selected for analysis (Table 1) exhibit small differences in tones and intensity of coloration. They all scattered light when probed with a narrow laser beam by, presumably, a second phase. For comparison, a sample of single-crystal pink quartz (GRR-1790a) with no turbidity, and a sample of dumortierite from Dehesa, California (GRR 122), were also analyzed. The quartz and dumortierite were crushed to grain sizes of 1–5 mm, cleaned successively in methanol, near-saturated oxalic acid, 2 N HCl and water. After cleaning, samples were left overnight in an oven at 90 °C to dry. The visual

**TABLE 1.** Sample locations and descriptions

Sample ID	Location, City	State, Country	Type of deposit (if known)
GRR-1790a*	Alto da Pitorá, Galileia	Minas Gerais, Brazil	Pegmatite
GRR-1811	Anza Valley	California, USA	Weathered pegmatite
GRR-1815		Madagascar	Pegmatite
GRR-1818		Namibia	Pegmatite
GRR-1819	Olivera dos Brejinhos	Bahia, Brazil	
GRR-1820	Scott Mine, Custer	South Dakota, USA	Massive vein
GRR-1821	Tobacco Root Mnts	Montana, USA	Massive vein
GRR-1822	Ramshorn Gulch, Tobacco Root Mnts	Montana, USA	Massive vein
GRR-1845	Miass	Ural Mnts, Russia	Pegmatite
GRR-1855	Custer	South Dakota, USA	Pegmatite
GRR-1856c	Shirley Meadows, Kern County	California, USA	Massive vein
GRR-1861		Bahia, Brazil	
GRR-1864	Joai'ma	Minas Gerais, Brazil	
GRR-1871	Obrazek Quarry, Pisek	Czech Republic	Granitic Pegmatite
GRR-1874	Lavra Schupp, Joai'ma	Minas Gerais, Brazil	
GRR-1877	Bedford	New York, USA	Pegmatite
GRR-1885	Madeleine, La Toma	San Luis, Argentina	Massive vein
GRR-1896	Gronoy	Nordland, Norway	Granitic pegmatite
GRR-1897	Amdal	Aust-Agder, Norway	Granitic pegmatite
GRR-1899	Samiresy, Antsirabe	Madagascar	
GRR-1900	Tsaramanga (Tongafeni), Mahaiza	(Fivondronana) Betafo, Madagascar	
GRR-1903	Rossing Berge	Namibia	
GRR-1904	Tammela	Finland	Granitic Pegmatite
GRR-1905	Ilvafjord, Julianehab Fjord	Greenland	
GRR-1906	Rabenstein	Bayern, Germany	Granitic Pegmatite
GRR-1907		China	
GR-7	Schinder Mine, Riverside County	California, USA	Granitic Pegmatite
GR-8	Feno Mine, Riverside County	California, USA	Granitic Pegmatite
CIT-2998	Santa Cruz County	Arizona, USA	
CIT-10416	Washoe County	Nevada, USA	

\* This specimen is the single-crystal pink quartz.

intensity of the coloration did not change during sample preparation and heating. The quartz samples were then dissolved in hot (100 °C) concentrated (48%) HF. All 29 massive quartz samples produced an insoluble fibrous residue (between 50 and 150 ppm of initial sample weight), with a color visually corresponding to the initial coloration of the samples. Residues from dissolution were treated with a 3:1 mixture of concentrated HF and HNO<sub>3</sub> and washed several times (until no visible fluorides were left) in 5% HNO<sub>3</sub> and H<sub>2</sub>O followed by centrifugation. Residues were dried on a hot (150 °C) plate. Upon drying, all samples (with the exception of GRR-1790a) produced residues of visually homogeneous, fine textured, flaky pink-colored mats. Sample GRR-1790a dissolved entirely. The dumortierite sample from Dehesa, California, did not experience significant weight loss after acid digestion. This acid-treated dumortierite sample is compared below to the resistant residues from quartz.

### Analytical methods

Imaging and qualitative analysis were performed with Caltech's CAMSCAN Series II scanning electron microscope and associated Link thin-window SiLi detector and EDS analyzer system. Semi-quantitative X-ray fluorescence spectra of all the fiber mats were taken with a Kevex/IXRF 770 EDS system using Ge and Gd secondary targets.

For the XRD analyses, fibers from GRR-1815 and dumortierite (Dehesa, California) were finely ground and loaded on the tip of a glass fiber. Conventional powder diffractometry was not used for two reasons: first, the available sample size was too small, and second, even our finest grinding of the sample produced particles with a very high length to width ratio, minimizing X-ray incidence in the elongated direction of the crystals. X-ray diffraction patterns were obtained with a 57.3 mm diameter Gandolfi camera that introduces 2 axes of rotation to the fibrous sample to ensure a powder diffraction pattern. The films were read with an estimated accuracy of 0.02° in the 2-theta measurements.

Infrared reflectance spectra of all fiber samples and dumortierite were obtained with a Nicolet 60SX FTIR spectrometer. Whole mats of fibers were first placed over a pinhole aperture. Spectra were then obtained with a NicPlan IR microscope at 4 cm<sup>-1</sup> resolution at near-normal incidence in the reflection mode. In addition, IR transmission spectra from samples GRR-1815, GRR-1811 and GRR-1864 dispersed in KBr pellets were obtained.

A Renishaw 1000 micro-Raman spectrometer with a 2 cm<sup>-1</sup> resolution was used to obtain Raman spectra of dumortierite and fiber samples. Five samples were examined. Mats of fibers were placed at the microscope focus (20×) and probed with a polarization-scrambled 514.5 nm laser operating at 50 mw.

Optical spectra were obtained using a home-built 1024 element silicon diode-array spectrometer. Spectra of the fiber mats were taken in a reflectance mode by focusing an approximately 2 mm diameter spot of light on the mat and collecting the reflected light at 90° to the incident light. These spectra were compared to massive rose quartz spectra obtained in a diffuse transmission mode. In these experiments light was directed into a rectangular block of rose quartz and light was collected from an adjacent face and directed to the spectrometer. Milky quartz was used as a reference standard in both of these experiments.

## RESULTS

### Physical characteristics

All massive rose quartz samples produced fibrous residues that, among different samples, varied from only slightly pink to bright pink. Clusters of parallel fibers show strong pleochroism under the optical microscope. They are bright pink parallel to the direction of elongation and near-colorless perpendicular to that direction.

### SEM observations and sample chemistry

Fiber samples obtained from dissolution experiments were examined with SEM. Representative back-scattered electron images of the fibers are shown in Figure 1. The length of the fibers was probably controlled by the grinding of the initial quartz sample. Figure 1b shows a more detailed image of a fiber cluster from the same sample from the Black Hills, South Dakota. The width of individual fibers recovered from different samples generally varied between 0.1 to 0.5 μm. The SEM-EDS analyses of the wide (relative to the width of individual crystals) areas of the fiber mats show an aluminosilicate framework with traces Ti and Fe in all samples. The relative intensity of the Al and Si peaks is approximately 2:1. Unfortunately, because of the small size of the individual fibers, quantitative analysis could not be obtained by EDS. No other elements were detected by EDS XRF. In particular, Sb, Ta, Nb, and As were absent even though they are found in holtite, a phase related to dumortierite (Hoskins et al. 1989).

An attempt to obtain chemical analyses of fibrous residues with ICP-MS (Elan 5000A) was also made. Residues were dissolved in 10N KOH. The ICP-MS analysis confirmed that boron was present in the fibers at levels of at least 2%, but repeat analyses did not yield reproducible results, presumably as a result of boron loss during the analytical procedure.

Occasional larger tabular crystals were observed in the fiber mats extracted from GRR-1819 and GRR-1820. A Si-Al matrix and morphology of these crystals suggest an Al<sub>2</sub>SiO<sub>5</sub> polymorph, probably sillimanite.

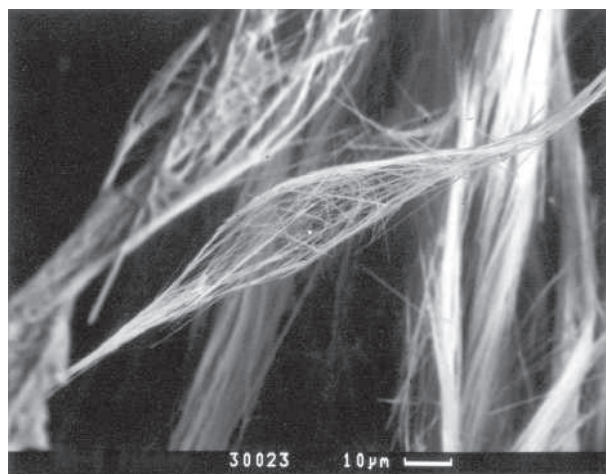
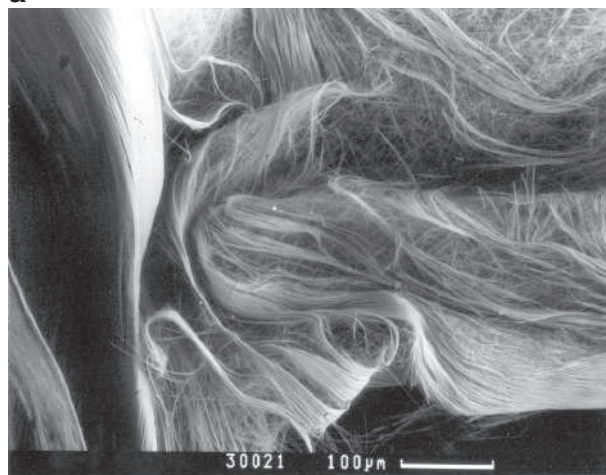
### X-ray diffraction

The ten most intense lines for fibers extracted from sample GRR-1815 (Madagascar) and dumortierite (Dehesa, California) are compared (Table 2) with those of the ICDD standard dumortierite (12-0270). The *d*-spacings from the diffractograms of the powdered fibers and natural dumortierite are close to those of the JCPDS standard dumortierite pattern, although there are differences in intensities.

### FTIR spectrometry

The IR spectra of the rose fibers are generally compatible with the spectrum of dumortierite (Fig. 2). All samples show band at 1450 cm<sup>-1</sup> that indicates the presence of the BO<sub>3</sub><sup>3-</sup> ion. Comparison of the absorption spectra of dumortierite and the fibers suggests that these phases have approximately the same borate to silicate ratios. The spectrum of dumortierite from Dehesa, California, closely matches the synthetic dumortierite spectrum (e.g., sample B12) of Werding and Schreyer (1990), but these spectra consistently differ from those produced by the various fiber samples. Relative band intensity differences in the 1000

a



**FIGURE 1.** SEM backscattered-electron images of the purified fibrous residue obtained after dissolution of rose quartz. (a) sample GRR-1820 (Custer, South Dakota), low resolution image showing the large length-to-width ratio of the fibers; (b) sample GRR-1820, higher resolution of a separate cluster of fibers. Individual fibers in this strand are about 100 nm wide.

and 500–600  $\text{cm}^{-1}$  regions are the salient differences.

### Raman spectrometry

Raman spectra of a dumortierite crystal and acid-treated powder (Fig. 3a and 3b) are similar, with only minor differences in the relative intensities of two bands in the 500–600  $\text{cm}^{-1}$  region. These differences can be attributed to the anisotropy of the single dumortierite crystal, as the spectrum was taken with the incident light perpendicular to the *c*-axis. The spectra produced by the fibers (Fig. 3c–e) are virtually identical to each other, but they are significantly different from the spectra generated by dumortierite.

### Optical absorption

Optical absorption spectra of fiber mats from GRR-1815, GRR-1818, GRR-1820, and GRR-1874 were compared to the

**TABLE 2.** XRD data\*

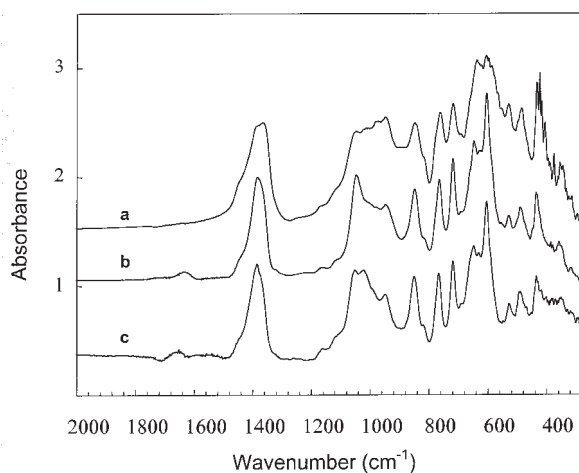
ICDD 12-0270	Dumortierite (Dehesa, CA)	GRR-1815	hkl
5.85 (100)	5.84 (100)	5.87 (100)	1 3 0
5.06 (90)	5.07 (85)	5.06 (85)	1 4 0
4.26 (50)	4.27 (60)	4.25 (50)	1 1 1
3.84 (50)	3.83 (55)	3.83 (45)	2 4 0
3.43 (60)	3.43 (85)	3.44 (85)	2 2 1
3.22 (60)	3.21 (80)	3.15 (50)	2 3 1
2.91 (60)	2.90 (75)	2.90 (50)	2 6 0
2.54 (20)	2.54 (55)	—	4 4 0
2.09 (80)	2.09 (90)	2.08 (90)	3 7 1
1.33 (50)	1.34 (70)	1.33 (50)	1 12 2

\* d-spacings are in angstroms, relative intensity in parenthesis are in percents.

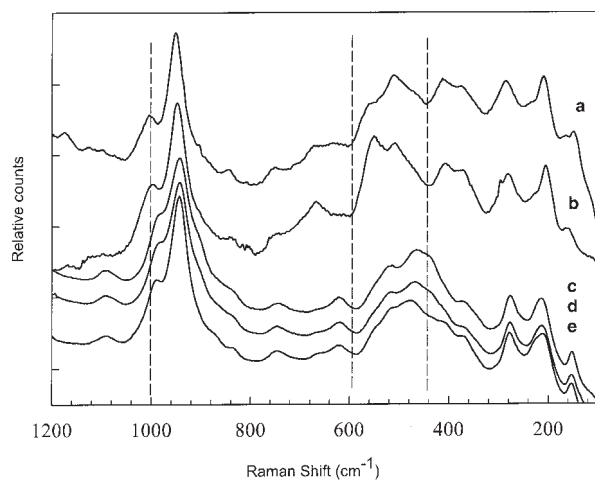
spectra of the corresponding initial rose quartz samples. The spectra of fiber mats showed an absorption band centered at approximately 500 nm. Moreover, the absorption bands of mats and their rose quartz precursors were nearly identical, indicating that their colors share a common origin (Fig. 4). For comparison, an optical spectrum of pink dumortierite (Dehesa, California) is also presented. In addition to the 500 nm band, it also has a longer wavelength shoulder arising from a second component previously described in Platonov et al. (2000).

### Irradiation and thermal stability of color

As noted earlier, the heating experiments by Ignatov et al. (1990) showed that their rose quartz and its associated clusters of fibrous inclusions in the quartz lose their color at ~ 500 °C. For several minerals, color loss on heating is associated with radiation-induced colors. Because rose quartz occurs in pegmatites, where a number of minerals such as smoky quartz have radiation-induced color, it is plausible that the pink color of rose quartz was developed upon natural irradiation within the pegmatite body. To explore this possibility, we heated quartz



**FIGURE 2.** FTIR spectra of (a) natural dumortierite (Dehesa, California), and (b) fibrous material from sample GRR-1815 (Madagascar) before, and (c) after the heating as described in the text. The intensity differences observed in the ~1000 and 500–600  $\text{cm}^{-1}$  regions between the standard and the fibers were observed in the spectra of all fibers examined.



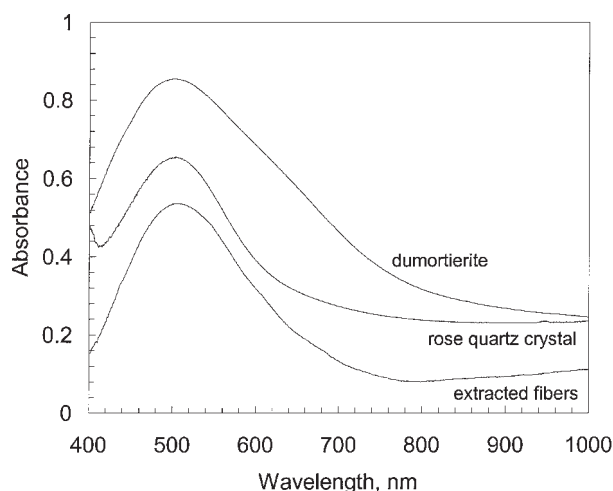
**FIGURE 3.** Raman spectra of (a) dumortierite (Dehesa, California) crystal, (b) dumortierite (Dehesa, California) acid-treated powder; and fibrous mats from the samples (c) GRR-1811, (d) GRR-1815, and (e) GRR-1861. Vertical dashed lines help to illustrate differences in the positions and intensities of the bands. The spectra of fiber samples are nearly identical, whereas the apparent differences in the 350–600  $\text{cm}^{-1}$  region between the dumortierite standard and the fibers are observed.

sample GRR-1815 for three weeks at 750 °C in air. The quartz sample lost its rose color, although the overall turbidity of the quartz did not visually increase. The fibrous inclusions extracted from the heated quartz were colorless. The FTIR spectrum of the colorless fibers was virtually identical to the spectrum of the pink fibrous residue from an unheated aliquot of the same rose quartz (Fig. 2) and indicates that a phase change did not occur. The colorless fibers then were irradiated in a  $^{137}\text{Cs}$  source. After exposure to 10 Mrad of gamma radiation, the fibers did not turn pink, suggesting that a radiation-induced center is not a cause of the color.

After ruling out the irradiation hypothesis, we designed several heating experiments to determine if this loss of color was due to the oxidation of transition elements. Experiments were performed on fibers extracted from 13 of the 29 samples studied. All 13 samples of rose fibers lost their color upon heating in air at temperatures between 430 and 750 °C. The higher the temperature, the more quickly the fibers lost their color. At 750 °C it takes few minutes, whereas at 430 °C it takes several days. The colorless fibers were reheated at the same temperatures under highly reducing conditions with a mixture of 95%  $\text{N}_2$  and 5%  $\text{H}_2$ . Eleven out of 13 samples regained their pink color. Samples GRR-1897 and GRR-1904 remained white. Both of these samples contained thicker fibers ( $\sim 1 \mu\text{m}$ ), so the reaction kinetics might be slower than for the other samples. No phase transitions occurred during the reduction experiments.

## DISCUSSION AND CONCLUSIONS

Our work confirms previous observations of aluminosilicate fibers in rose quartz and extends it to numerous localities around the world. After separation from the host quartz, these insoluble fibers are the same color as the initial rose quartz. Thus, we ar-



**FIGURE 4.** The optical absorption spectra of the extracted fibrous mat and corresponding crystal of rose quartz from GRR-1815 (Madagascar). The two spectra, offset vertically for clarity, both have an absorption band at about 500 nm. The spectrum of dumortierite from Dehesa, California, is shown for comparison.

gue that the color of rose quartz itself arises from these fibrous inclusions. Several experiments indicate that these fibers are related to dumortierite. However, there are significant differences between their spectroscopic signatures and those of dumortierite. Nevertheless, dumortierite remains a valid point of comparison to the properties of these fibers.

Dumortierite itself is commonly associated with quartz in hydrothermal and pegmatitic environments. It is common for dumortierite to contain traces of Fe and Ti which are associated with its color (Alexander et al. 1986). An absorption band in the dumortierite spectrum centered at about 500 nm has been attributed to  $\text{Fe}^{2+}\text{-Ti}^{4+}$  IVCT by Ignatov et al. (1990) who also associated the color of dumortierite in association with rose quartz to the color of their sample of rose quartz. Our work supports their proposal for the origin of rose color in dumortierite.

Because the fibers we recovered from rose quartz always show traces of Ti and Fe, we propose that the same Fe-Ti charge transfer mechanism operates in the dumortierite-related fibrous phase extracted from rose quartz. Smith et al. (1978) had previously proposed that a Fe-Ti charge transfer mechanism is responsible for the color of rose quartz but thought that it originated with substitutional components within the quartz itself. Heating experiments in open air showed that the fibers could easily be rendered colorless. Because we were able to return color to the fibers by heating them under reducing conditions, we believe that oxidation and reduction of iron ( $\text{Fe}^{2+} \leftrightarrow \text{Fe}^{3+}$ ) in Fe-Ti IVCT centers are responsible for the change of the fiber color from pink to colorless and back. Hemingway et al. (1990) speculated that the color change that occurs in dumortierite may reflect oxidation of iron and loss of charge transfer among  $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$ , and  $\text{Ti}^{4+}$  rather than dumortierite decomposition. Our experiments demonstrate this mechanism in the fibers.

Our FTIR study of fibers extracted from rose quartz after

heating to 750 °C showed that the fibers remained structurally unaltered, even though dumortierite reportedly decomposes above ~ 700 °C at atmosphere pressure (Werdning and Schreyer 1996).

Ignatov et al. (1990) showed that the color of quartz with the macroscopic dumortierite inclusions is stable below 500 °C at 1 atm and does not depend on the duration of the heating. By contrast, our heating experiments revealed that there is a time dependence to the color stability of the heated fibers. Fibers lose their color within a few hours when heated at 500 °C, whereas decoloration takes several days at 430 °C.

### Fading of rose quartz

The stability of the color of the fibers appears inconsistent with the often reported fading of the color of some fraction of rose quartz after prolonged exposure to the sun in mine dumps. We have not observed this process in any of our samples and have no direct experimental results to bear on this problem. We speculate that the photo-oxidation of iron in the fibers is a plausible but unlikely process. It is further possible, but unproven, that common massive rose quartz could contain a component of the photosensitive phosphorous center found in crystalline pink quartz. This would not explain the lore that some faded rose quartz regains its color when soaked in water. Another, more conservative, explanation for the fading of massive rose quartz would be the solar heat-induced expansion and shattering of CO<sub>2</sub> inclusions causing microfractures and scattering of light near the surface of the quartz.

### Origin of the fibers

The origin of the fibers is, in part, related to the origin of rose quartz. A study of primary fluid inclusions in the rose quartz from Black Hills, South Dakota (the locality of the sample GRR1820), shows that crystallization of the quartz occurred in the temperature range 400 to 450 °C, at 3.5 to 4 kbars pressure (Sirbescu and Nabelek 1997; Sirbescu, personal communication, 1998). Because these temperatures are in or near the temperatures at which the rose color was lost in our heating experiments, it seems unlikely that the pink fibrous phase was captured during the growth of the quartz.

Another scenario is that an initially colorless fibrous phase grew within quartz and rose color was gained after crystallization. The lack of response of the colorless fibers to irradiation appears to rule out color generation from a radiation-induced color center. Sirbescu's (personal communication, 1998) work shows that the composition of the primary inclusions in this quartz is mainly CO<sub>2</sub> with minor CH<sub>4</sub>. While the latter indicates plausible reducing conditions in the fluid during the quartz crystallization or crystallization of the inclusions that might affect the oxidation state of Fe, this scenario also seems unlikely.

Our favored explanation is that the pink fibrous phase exsolved from crystallized quartz at temperatures below 430 °C. There are many reports of asterism in rose quartz. The most detailed was that of Kalkowsky (1915–1920). The asterism in rose quartz implies orientation of fibers perpendicular to *c* axis and along three equivalent crystallographic directions, which, presumably, is diagnostic of exsolution.

Fine differences between the FTIR and Raman spectra of the

fibers and dumortierite could also be due to the presence of an impurity phase. For example, the fibrous mineral inclusions could be a mixture of true dumortierite and a related phase. To address these questions, a more detailed HRTEM and AEM investigation of the chemistry and structure of individual crystals of these fibers is in progress (Chi Ma et al., in preparation).

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### REFERENCES CITED

- Alexander, V.D., Griffen, D.T., and Martin T.J. (1986) Crystal chemistry of some Fe- and Ti-poor dumortierites. *American Mineralogist*, 71, 786–794.
- Applin, K.R. and Hicks, B.D. (1987) Fibers of dumortierite in quartz. *American Mineralogist*, 72, 170–172.
- Bailey, P. and Well, J. (1991) EPR study of the [SiO<sub>2</sub>/Li]<sup>o</sup> centre in a-Quartz. *Journal of Chemical Society, Faraday Transactions*, 87(19), 3143–3146.
- Balitsky, V.S., Makhina, I.B., and Emelchenko A.G., et al. (1996) Eksperimental'noe izuchenie usloviy obrazovaniya kristallov rozovogo fosforosoderzhashego kvarca i prichiny ego redkoy vstrechaemosti v prirode. *Geokhimiya*, 11, 1074–1081 (in Russian).
- Cassedanne, J.P. and Roditi, M. (1991) Crystallized and massive rose quartz deposits in Brazil. *Journal of Gemmology*, 22, 5, 273–286.
- Cohen, A.J. and Makar, L.N. (1984) Differing effects of ionizing radiation in massive and single crystal rose quartz. *Neues Jahrbuch für Mineralogie-Monatshefte*, 11, 513–521.
- — — (1985) Dynamic biaxial absorption spectra of Ti<sup>3+</sup> and Fe<sup>2+</sup> in a natural rose quartz crystal. *Mineralogical Magazine*, 49, 709–715.
- Dennen, W.H. and Puckett, A.M. (1971) On the chemistry and color of rose quartz. *Mineralogical Record*, 3, 226–227.
- Folk, R.L. (1989) Internal structuring of quartz as revealed by boiling concentrated hydrofluoric acid. *Journal of Geological Education*, 37, 250–260.
- Gordon, S.C. (1945) The inspection and grading of quartz. *American Mineralogist*, 30, 269–295.
- Hemingway, B.S., Anovitz, L.M., Robie, R.A. and McGee, J.J. (1990) The thermodynamic properties of dumortierite Si<sub>3</sub>B[Al<sub>6.75</sub>□<sub>0.25</sub>O<sub>17.25</sub>(OH)<sub>0.75</sub>]. *American Mineralogist*, 75, 1370–1375.
- Holden, E.F. (1924a) The cause of color in rose quartz. *American Mineralogist*, 9(4), 75–89.
- — — (1924b) The cause of color in rose quartz (concluded). *American Mineralogist*, 9(5), 101–108.
- Hoskins, B.F., Mumme, W.G., and Pryce, M.W. (1989) Holtite, (Si<sub>1.25</sub>Sb<sub>0.75</sub>)B[Al<sub>6</sub>Al<sub>0.43</sub>Ta<sub>0.27</sub>□<sub>0.30</sub>]O<sub>15</sub>(O,OH)<sub>2.25</sub>; crystal structure and crystal chemistry. *Mineralogical Magazine*, 35, 457–463.
- Ignatov, S.I., Platonov, A.N., Sedenko, V.S., and Taran, M.N. (1990) Pozheve zavravlennya kvarcu, zvyazane z mikrokvlyuchennyami dumortyeritu. *Dopovid Akademiya Nauk Ukrain's'koyi RSR, Seria B: Geologichni, Khimichni ta Biologichni Nauki*, 7, 23–26 (in Ukrainian).
- Kalkowsky, E. (1915–1920) Opalezierender Quarz. *Zeitschrift für Kristallographie und Mineralogie*, 53, 23–50 (in German).
- Lehmann, G. (1969) Zur Farbe von Rozenquarz. *Neues Jahrbuch für Mineralogie-Monatshefte*, 222–225 (in German).
- Maschmeyer, D. and Lehmann, G. (1983) A trapped-hole center causing rose coloration of natural quartz. *Zeitschrift für Kristallographie*, 163, 181–196.
- Moore, P.B. and Araki, T. (1978) Dumortierite, Si<sub>3</sub>B[Al<sub>6.75</sub>□<sub>0.25</sub>O<sub>17.25</sub>(OH)<sub>0.75</sub>]: A detailed structure analysis. *Neues Jahrbuch für Mineralogie Abhandlungen*, 132, 231–241.
- Platonov, A.N., Langer, K., Chopin, C., Andrut, M., and Taran, M.N. (2000) Fe<sup>2+</sup>-Ti<sup>4+</sup> charge-transfer in dumortierite. *European Journal of Mineralogy*, 12, 521–528.
- Rossmann, G.R. (1994) Colored varieties of the silica minerals. In P.J. Heaney, C.T. Prewitt, and G.V. Gibbs, Eds., *Silica. Physical Behavior, Geochemistry and Material Applications*, 29, p. 433–462. Reviews in Mineralogy, Mineralogical Society of America, Washington, D.C.
- Sirbescu, M.-L.C. and Nabelek, P.I. (1997) Fluid evolution in a simple pegmatite from the Black Hills pegmatite field, South Dakota. 1997 Annual Meeting, Abstracts with Programs, Salt Lake City, Utah, 29, p. 457–458. Geological Society of America.

- Smith, G., Vance, E.R., Hasan, Z., Edgar, A., and Runciman, W.A. (1978) A charge transfer mechanism for the colour of rose quartz. *Physica Status Solidi (A)* 46, K135-K140.
- Vultee, J. von (1955) Über die orientierten Verwachsungen von Rutil in Quarz. *Neues Jahrbuch Für Mineralogie-Abhandlungen*, 87, 389–415 (in German).
- Vultee, J. von and Lietz, J. (1956) Über die Rolle des Titans als Farbungsursache von Blau- und Rosenquarzen. *Neues Jahrbuch für Mineralogie-Monatshefte*, 49–58 (in German).
- Werding, G. and Schreyer, W. (1990) Synthetic dumortierite, its PTX-dependent compositional variations in the system  $Al_2O_3$ - $B_2O_3$ - $SiO_2$ - $H_2O$ . *Contributions to Mineralogy and Petrology*, 105, 11–24.
- — (1996) Experimental Studies on Borosilicates and Selected Borates. In E.S. Grew and L.M. Anovitz, Eds., *Boron: Mineralogy, Petrology and Geochemistry*, 33, p. 117–159. *Reviews in Mineralogy*, Mineralogical Society of America, Washington, D.C.
- Wright, P.M., Weil, J.A., Buch, T., and Anderson, J.H. (1963) Titanium colour centers in rose quartz. *Nature*, 197, 246–248.

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