

## Relationships between radiation damage and trace water in zircon, quartz, and topaz

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### ABSTRACT

The presence of trace amounts of water or hydroxide ion can dramatically affect the response of a mineral to radiation from both internal and external sources. In zircon, where radioactive decay of U causes structural damage (metamictization), water can enter the structure after a threshold of damage is reached and stabilize the metamict state by annealing local charge imbalance. Quartz crystals with both amethyst and citrine zones have molecular water in the citrine zones and dominantly hydroxide ion in the amethyst zones. This may be due to the reduction of the amethyst Fe(IV) color center by atomic H formed by radiolysis of the water. In topaz, special hydroxide sites correlate with the formation of a brown color center. The crystallographically identified hydroxyl on the (OH,F) site does not appear to be correlated with radiation damage. The mobility of H and the ease with which H-O species may be formed in silicates appear to explain much of the role of hydrous species in radiation-damage processes in minerals. These species occur in several charge states and may anneal local charge imbalance. The occurrence of trace amounts of water in even nominally anhydrous minerals makes this interaction common.

### INTRODUCTION

It is important to understand the mechanisms of radiation damage in minerals with regard to both radiometric age dating and radioactive waste storage. Processes observed in crystalline solids can also be applied to understanding those in glasses where a lack of structural information complicates the determination of radiation-damage mechanisms. In this paper we discuss the relationship between the potential for radiation damage in minerals and the presence of hydrous species.

Radiation damage in minerals may be divided into two categories, metamictization and oxidation-state changes. The distinction is not clear-cut, but metamictization may be considered to arise primarily from the structural damage caused by  $\alpha$ -particles and recoiling nuclei (Yada et al., 1981; Ewing and Headley, 1983). Oxidation-state changes can be caused by any type of ionizing radiation but need not be accompanied by the breaking of bonds or movement of nuclei in the structure. This second type of radiation damage is especially common in minerals that contain radioactive elements such as K or U or that have been in close contact with K-bearing minerals over long periods of time. <sup>40</sup>K is particularly significant because it is abundant in nature and the  $\gamma$ -ray emitted during its decay can penetrate several centimeters into adjacent minerals.

Studies in our laboratory have shown that hydrous com-

ponents in minerals are frequently correlated with radiation damage. This relationship also exists in glasses where in most cases the presence of the H species OH<sup>-</sup>, H<sub>2</sub>O, or H<sub>2</sub> inhibits the formation of color centers (Van Wieringen and Kats, 1957; Faile and Roy, 1970; Hartwig, 1976; Shelby, 1979). One color center, the E' center in fused silica, is positively correlated with the presence of hydroxyl groups (Weeks and Lell, 1964). However, when samples are both irradiated and observed at -195°C, even hydrous silica glass becomes radiation damaged (Arnold and Compton, 1959). Upon warming, the color centers are destroyed.

A similar temperature-hydroxyl relationship is observed in smoky quartz (see Weil, 1975, for a review). The smoky quartz color center is caused by the simultaneous displacement of an electron and an alkali ion from the vicinity of an Al ion. However, when the Al is charge-compensated by a proton instead of an alkali, the color center cannot form at room temperature because the proton diffuses back and destroys it. When irradiated at 77 K, Al-H centers can form smoky centers because proton diffusion is too slow (Mackey, 1963).

Hofmeister and Rossman (1985a) showed that both water and Pb<sup>2+</sup> must be present in feldspar in order for radiation to form the colored amazonite variety. They hypothesized that radiolysis of the water yields OH<sup>0</sup> radicals that oxidize the Pb<sup>2+</sup> yielding the chromophore, Pb<sup>3+</sup>. The water is regenerated through the reaction of H<sup>0</sup> radical with a hole center and the subsequent recombination of the H<sup>+</sup> and OH<sup>-</sup>. A second color center in feldspar, the smoky center, does not form if water is present. Hofmeister and Rossman (1985b) showed that this center is

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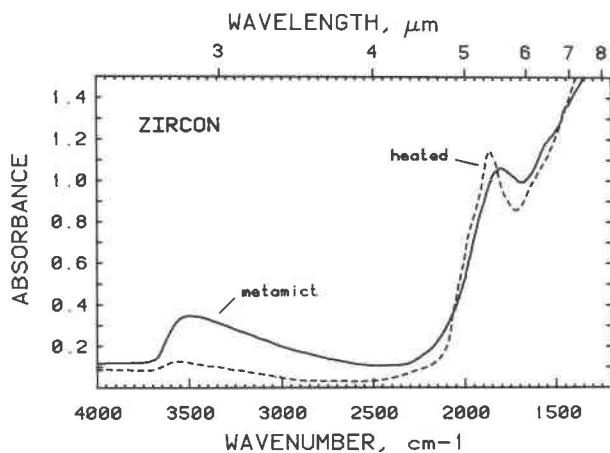


Fig. 1. IR spectrum of a metamict zircon from Sri Lanka containing 6500 ppm eU. Solid trace—spectrum of untreated sample; dashed trace—sample after being heated to 800°C for 4 h, causing partial dehydration and recrystallization. The broad band from 3650 to 2500  $\text{cm}^{-1}$  is due to  $\text{OH}^-$ . Sample thickness 0.307 mm.

similar to the smoky center in quartz and hypothesized that when water is present, its radiolysis yields  $\text{H}^0$  that diffuses and destroys the smoky center.

In this paper, we discuss three new examples of minerals in which the radiation-damage process is related to the presence of hydrous species. In some cases the water or hydroxyl appears to promote radiation damage, whereas it hinders it in others. We will indicate, however, that the mobility and reactivity of H species is the unifying factor.

#### EXPERIMENTAL METHOD

Water and hydroxyl concentrations and species identification were determined using infrared (IR) and near-infrared (NIR) spectroscopy, as described by Aines and Rossman (1984). Visible and NIR spectra were obtained with a CARY 17I spectrometer using calcite polarizers and techniques described by Amthauer and Rossman (1984). IR spectra were collected with a Perkin-Elmer 180 using techniques described by Rossman (1975) and Aines et al. (1984). A gold-wire polarizer was used for IR studies. Doubly polished single-crystal slabs were used for all measurements. Determination of H speciation was made according to the methods outlined in Aines and Rossman (1984).

#### RESULTS AND DISCUSSION

##### Zircon

Zircons from the stream gravels of Sri Lanka share a common origin but vary in U content from 20 to 8300 ppm equivalent U (eU). Nonmetamict samples, as judged by their X-ray powder pattern and both IR and optical anisotropy, contain less than 2000 ppm eU and have no detectable  $\text{H}_2\text{O}$  or  $\text{OH}^-$  in their IR spectrum. However, above 2500 ppm eU, the zircons are metamict and contain easily detectable  $\text{OH}^-$  (Woodhead, Rossman, and Silver, in prep.). The  $\text{OH}^-$  is indicated by a broad isotropic band with its maximum at 3500  $\text{cm}^{-1}$  in the IR spectra of single-crystal slabs (Fig. 1). These metamict samples also have

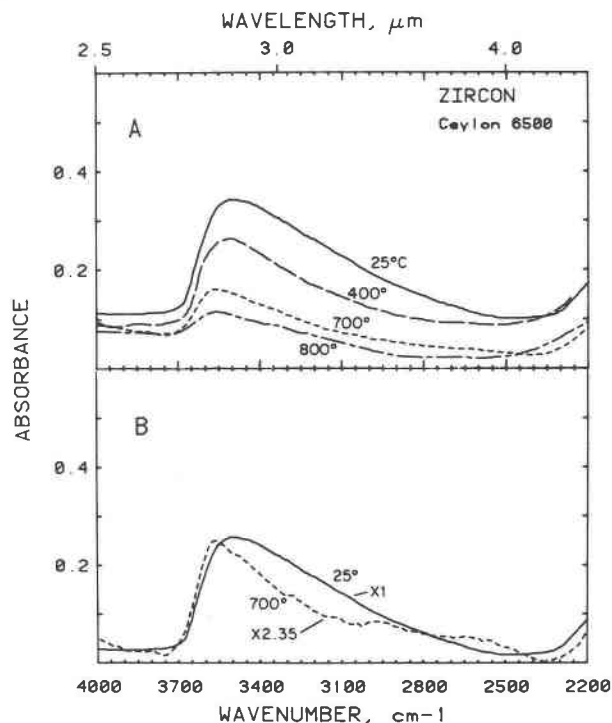


Fig. 2. (A) Single-crystal IR spectra of the same sample as in Figure 1 after cooling from the indicated temperature. (B) Comparison of the 25°C spectrum and the 25°C spectrum of the sample that was cooled from 700°C (Fig. 2a); the latter spectrum is scaled to have the same peak absorbance as the original 25°C spectrum.

broad isotropic bands below 2000  $\text{cm}^{-1}$  that replace the sharper, anisotropic bands seen in nonmetamict samples. There is no detectable band corresponding to the  $\nu_2$  bending mode of  $\text{H}_2\text{O}$  at 1650  $\text{cm}^{-1}$  which would be expected if the hydrous component were actually *molecular* water. From this we deduce that the speciation is as  $\text{OH}^-$ . The broad  $\text{OH}^-$  stretch near 3500  $\text{cm}^{-1}$  appears to be caused by hydroxyl groups in a range of structural environments.

Figures 2a and 2b show the behavior of the 3500- $\text{cm}^{-1}$  broad band after heating. Dehydration became rapid at 600°C; however, no recrystallization occurred (as judged by the growth of sharp zircon bands in the IR spectrum below 2000  $\text{cm}^{-1}$ ) until 700°C. Figure 2b shows the 700°C spectrum scaled to the same peak height as the 25°C spectrum to show that there is a distinct loss of intensity in the lower-energy side of the broad band. This indicates that the hydroxyl groups that are involved in shorter (stronger) H bonds are expelled preferentially (Aines and Rossman, 1984). The additional intensity at 2800–2400  $\text{cm}^{-1}$  is due to overtone vibrations involving  $\text{SiO}_4$  units. As recrystallization occurs, these modes increase in intensity.

The  $\text{OH}^-$  groups in this zircon appear to be involved in local charge balance of the disrupted lattice. Because these samples were not collected from their host rocks, the source is not definitely known. It appears that they all start out anhydrous and that water enters the structure

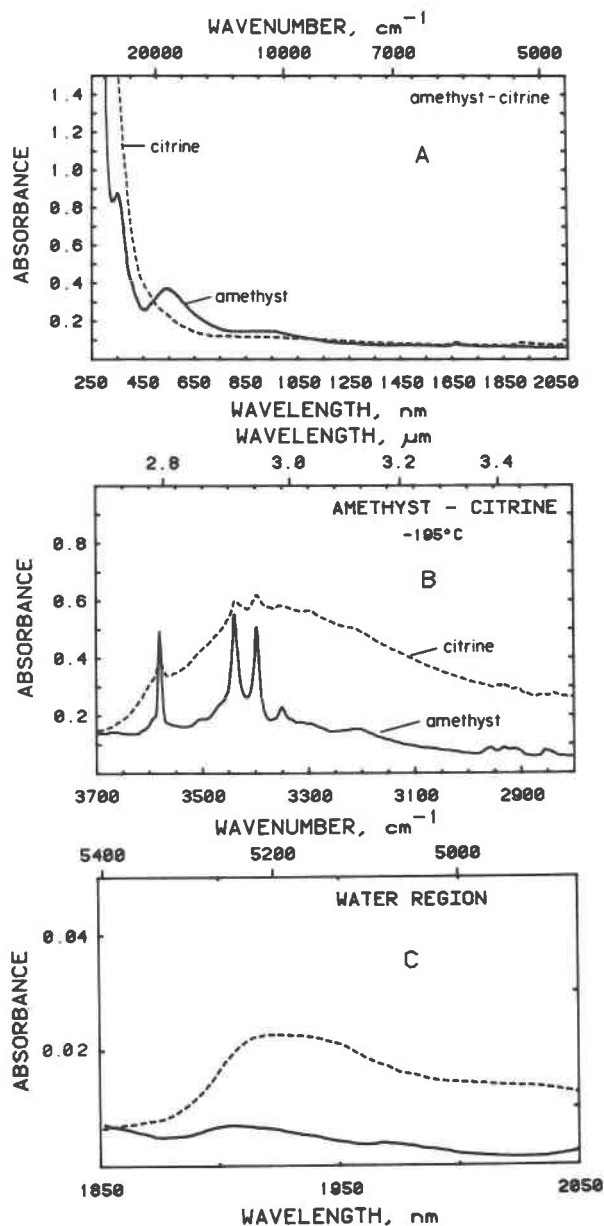
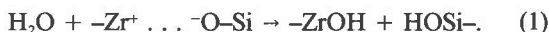


Fig. 3. (A) Brazilian amethyst-citrine single crystal. Unpolarized. Sample thickness 5.05 mm. (B) IR spectra of same zones in crystal, thickness 1.04 mm. Run at 77 K, polarized  $E \perp c$ . (C) Expanded view of NIR spectra in 3A, same conditions, showing the characteristic absorption due to molecular water in the citrine spectrum.

only after a threshold of radiation damage (metamictization) is reached. We believe that molecular water enters the crystal and then dissociates to form hydroxyl groups that satisfy local charge requirements. One possible reaction would be



These  $\text{OH}^-$  groups should exist in a number of structural environments that would give the broad band absorption in the IR spectrum. During recrystallization the water reforms and is expelled, with the hydroxyl groups involved in shorter H bonds being expelled first. Most of the water is lost before any recrystallization becomes apparent in the IR spectrum (shown by the growth of sharp overtones of crystalline zircon near  $1900 \text{ cm}^{-1}$ ), indicating that water is actually stabilizing the metamict state.

#### Quartz: Amethyst-citrine

Ionizing radiation produces the gray smoky and purple amethyst varieties of quartz as well as a citrine-like yellow variety. All three colors are strongly linked to the presence or absence of hydrous impurities. The origin of smoky quartz is well known (Weil, 1975) and will not be discussed further. Amethyst coloration is known to be caused by the formation of  $\text{Fe}^{4+}$  centers from  $\text{Fe}^{3+}$  by ionizing radiation (Cox, 1976, 1977). However, the intensity of coloration is not a simple function of Fe concentration (Dennen and Puckett, 1972; Lehmann and Bambauer, 1973). No change in the IR spectrum of quartz accompanies the formation of the  $\text{Fe}^{4+}$  centers, and no  $\text{Fe}(\text{H})$  defect analogous to the  $\text{Al}(\text{H})$  defect has been identified (Kats, 1962; Chakraborty and Lehmann, 1978).

Citrine coloration can arise from several mechanisms. The citrine most commonly encountered is actually amethyst that was heated to  $300\text{--}500^\circ\text{C}$  causing the Fe in the amethyst to precipitate into small clusters of iron oxides which cause a yellow-brown color (Stock and Lehmann, 1977). True citrine is caused by incorporation of  $\text{Fe}^{3+}$  in quartz with appropriate charge compensation. A citrine-like coloration can also be caused by irradiation of quartz and has been associated with a high content of Li as an impurity (Maschmeyer et al., 1980; Bukanov and Markova, 1969).

A particularly dramatic example of colored quartz is single-crystal amethyst-citrine reportedly occurring in Brazil near the Bolivian border. This material contains alternating sections of amethyst and citrine color. The boundary between any two color zones is optically sharp and planar. The amethyst and citrine colors occur under the  $r\{10\bar{1}1\}$  and  $z\{01\bar{1}1\}$  faces, respectively (Koivula, 1980). Because the entire crystal should have received the same exposure to ionizing radiation from the natural environment, it is of interest to determine why only certain sectors have developed amethyst color.

Figure 3 shows vis, NIR, and IR spectra of the amethyst-citrine. Figure 3a shows that the amethyst color is caused by an absorption at 550 nm typical of amethyst. The citrine color is caused by the broad tail of an absorption in the ultraviolet region which peaks at about 240 nm (off scale in Fig. 3). Figure 3b shows that there is a remarkable difference between the two zones in the IR spectra. The citrine zone is dominated by a broad, isotropic band that is absent in the amethyst zone. This broad band correlates with absorption in the 1900-nm region which is characteristic of the  $\nu_2 + \nu_3$  combination mode of molecular water

(Fig. 3c) and is due to small groups of water molecules trapped during rapid crystal growth (Aines et al., 1984). These groups are not large enough to be considered fluid inclusions, probably ranging in size from about five to several hundred molecules.

The exact geologic occurrence of the Brazilian amethyst-citrine and possible commercial treatments have not been revealed. Thus we have examined the color and H<sub>2</sub>O relationships in a quartz crystal suite of known origin. These samples are found in quartz veins in deeply weathered granitic rock near Hyderabad, India, and have not been subject to any commercial treatment (R. H. Currier, pers. comm.). These crystals contain a number of amethyst and citrine zones. These samples also indicate that amethyst color occurs in the zones with the least molecular water. Figure 4 shows the inverse correlation between absorption at 550 nm (amethyst color) and absorption at 1920 nm (molecular H<sub>2</sub>O) for the Indian and Brazilian samples. In the Indian samples, amethyst and citrine areas can occur in either the *r* or *z* sector. The H<sub>2</sub>O correlation, however, holds for both sectors. Amethyst only occurs in low H<sub>2</sub>O zones. The minimum H<sub>2</sub>O concentration for the Indian samples appears to correspond to a background due to visible fluid inclusions (water groups much larger than those previously discussed) that are present in varying amounts in this material.

Maschmeyer et al. (1980) noted that intensity of radiation-induced citrine color was correlated to the Li content as estimated by the intensity of the Li(H) IR absorption at 3396 cm<sup>-1</sup>. In the Brazilian amethyst-citrine samples we studied, this peak is clearly less intense in the citrine sector than in the amethyst sector.

Additional information comes from efforts at producing synthetic amethyst. In order to obtain flawless amethyst by irradiating Fe<sup>3+</sup>-containing synthetic quartz with  $\gamma$ -rays, the initial crystals must be grown slowly (0.3–0.8 mm/d) and in a Na-free solution (Balitsky, 1977). Under these same slow growth rates (350°C, basal growth) synthetic quartz grown at Bell Laboratories incorporates the minimum amount of a hydrous component (Kirby, pers. comm.). Aines et al. (1984) have shown that the hydrous component is essentially entirely hydroxyl when Na is absent, and that when Na is incorporated, there is the additional incorporation of molecular water. In the latter crystals, the ratio of molecular water to Na is 5:1. Apparently, the successful amethyst-growth technique (Balitsky, 1977) involves complete elimination of molecular water from the amethyst starting material.

Our study suggests that the formation of the amethyst color center is suppressed by the presence of molecular water. In direct analogy to the mechanical weakening of quartz by molecular water (Aines et al., 1984), the water involved here must occur in small reactive groups and not in fluid inclusions. The inverse correlation between amethyst color and molecular water may be explained by the hypothesis that radiolysis of water produces atomic H that may freely move through the quartz reducing the Fe<sup>4+</sup> color centers to Fe<sup>3+</sup> essentially as fast as they are

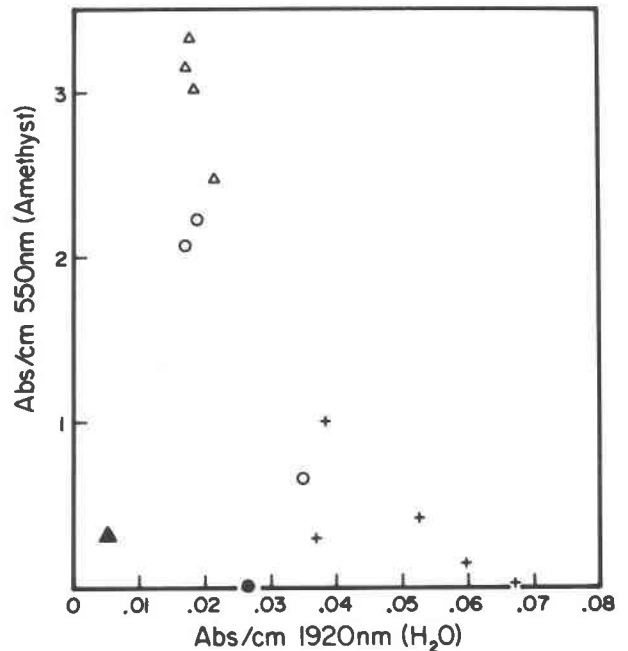


Fig. 4. Relationship between peak intensity at 550 nm (corresponding to amethyst color) and 1920 nm (molecular H<sub>2</sub>O) for amethyst-citrine. Measured using unpolarized light. 550-nm baseline drawn from 450 to 700 nm as a straight line, 1920-nm baseline from 1870 nm to 2100 nm. Open symbols, Indian quartz: triangle—amethyst zone in a growth sector containing only amethyst; cross—citrine zone in a growth sector containing only citrine; circle—amethyst or colorless in a sector containing citrine. Filled symbols, Brazilian samples (Fig. 3): triangle—amethyst zone; circle—citrine zone.

formed. The production of molecular hydrogen, H<sub>2</sub>, through water radiolysis is well known (e.g., Dragnić, 1971, p. 38), and atomic hydrogen, H<sup>0</sup>, has been detected by EPR in synthetic quartz (Weeks and Abraham, 1965), natural rose quartz (Rinnenberg and Weil, 1972), synthetic CaF<sub>2</sub> (Hall and Schumacher, 1962), and brazilianite (Hill and Lehmann, 1978). The H was unstable above 77 K in all cases except in the brazilianite where it can persist to 450 K. The low stability of atomic H in quartz is most certainly a function of its extreme reactivity and mobility. However, the water from which atomic H is formed must apparently be dispersed throughout the mineral and not in fluid inclusions that can trap the radicals produced by radiolysis. The effort to synthesize amethyst was successful when molecular water was completely excluded, eliminating H formation during irradiation. Likewise, in the natural amethyst-citrine samples, our results suggest that amethyst cannot form where too much molecular water is present.

Fe<sup>3+</sup> can enter quartz in both substitutional and interstitial sites, not all of which are precursors for amethyst coloration. Experiments by Nassau (1981, pers. comm.) indicate that the appropriate precursor Fe<sup>3+</sup> sites are present in the citrine zones of the amethyst-citrine from Brazil. He has shown that the amethyst-citrine can be heated to

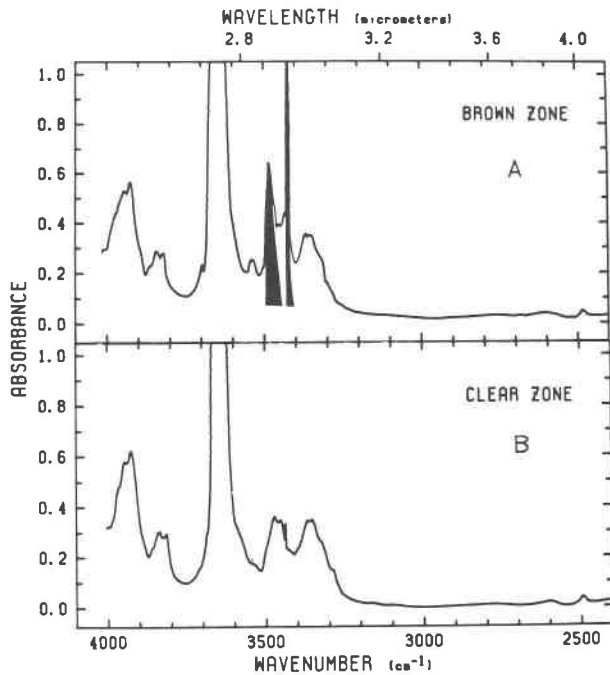


Fig. 5. Comparison of brown (A) and colorless (B) zones in an irradiated Brazilian topaz. Polarized in  $\alpha$  direction, sample thickness 0.70 mm. Run at 307 K. The peaks unique to the brown zone are shown in black. The majority of the peaks at 3300–3500  $\text{cm}^{-1}$  have “mirror image” peaks at 3800–4000, indicating that they are sum and difference modes on the 3680- $\text{cm}^{-1}$  fundamental. The difference modes (3300–3500  $\text{cm}^{-1}$ ) are suppressed at  $-195^\circ\text{C}$  (see Fig. 8).

400°C to remove the amethyst color in the  $r$  sectors and irradiated to restore it only in the  $r$  sector. In each case the citrine color was unchanged. When he heated it to 550°C, the amethyst color was again lost from the  $r$  sector, but when it was irradiated, both the  $r$  and  $z$  sectors gained amethyst color. This observation suggests that by heating to 550°C, water in the originally citrine zones either is lost or, more likely, moves to form larger aggregates of water (fluid inclusions) and is thus no longer available to block the formation of the amethyst color.

### Topaz

Irradiation can commonly produce two colors in initially colorless topaz: brown and blue. There is a strong correlation between the brown color and anomalous OH sites. Topaz contains one crystallographically defined (OH $^-$ , F $^-$ ) site (Ribbe and Gibbs, 1971) and should yield an IR spectrum containing one peak due to hydroxyl. However, it is common for topaz to exhibit a number of absorption bands in the O–H stretching region, and some of these bands correlate with the intensity of brown coloration in zoned, irradiated samples (Fig. 5). The anticipated stretching mode is at 3650  $\text{cm}^{-1}$ , and the anomalous peaks occur at 3460 and 3425  $\text{cm}^{-1}$ . The remainder of the absorptions are sum and difference modes centered on the 3650- $\text{cm}^{-1}$  fundamental; the low-frequency set

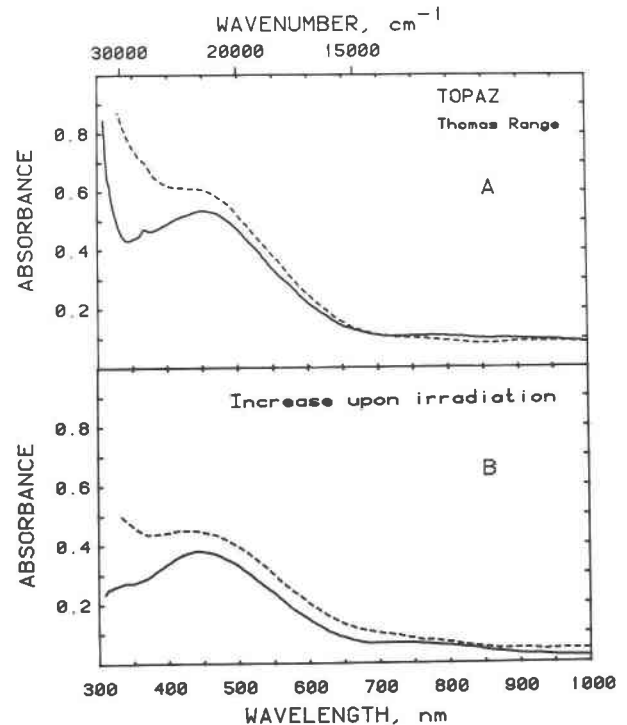


Fig. 6. (A) VIS-NIR spectra of natural brown topaz from the Thomas Mountains, Utah, rhyolitic tuff. Solid trace— $\beta$  polarization; dashed trace— $\alpha$  polarization. Sample thickness 7.00 mm. (B) Spectrum of the component that grows when the sample is irradiated with 21.7 Mrads of  $^{137}\text{Cs}$   $\gamma$ -rays. The original spectrum (Fig. 6A) has been subtracted from that of the irradiated sample.

disappears when cooled to 77 K. The remaining topaz spectra in this paper were obtained at 77 K.

The brown coloration in natural topaz from the Thomas Mountains rhyolite (Utah) is due to two components in the optical spectrum, a peak at 460 nm and a broad tail extending from the ultraviolet (UV) region into the visible region (Fig. 6a). The detailed origin of these components has not been established. Additional irradiation of this brown topaz causes an increase in both the 460-nm band and the UV tail; the increased components are shown in Figure 6b. The Thomas Mountains samples are fluoride rich, and accordingly hydroxyl poor. The anticipated fundamental OH $^-$  absorption at 3650  $\text{cm}^{-1}$  is dominated by anomalous absorptions in the 3400–3450- $\text{cm}^{-1}$  region (Fig. 7a). The IR spectrum undergoes a marked change after irradiation, with the peaks in the 3400–3450- $\text{cm}^{-1}$  region undergoing a net decrease in intensity, although one component at 3440  $\text{cm}^{-1}$  increased (Fig. 7b). There was no net change in the intensity of the 3650- $\text{cm}^{-1}$  fundamental.

In order to expand these observations, we studied a commercially electron-irradiated topaz from Brazil containing two shades of brown and a light-blue zone. As is usual in irradiated topaz, the boundaries between the colors are sharp and planar. In the crystal, all the color boundaries are coplanar with the prism faces of the sample. The VIS-NIR spectra after irradiation are shown in Figure 8a.

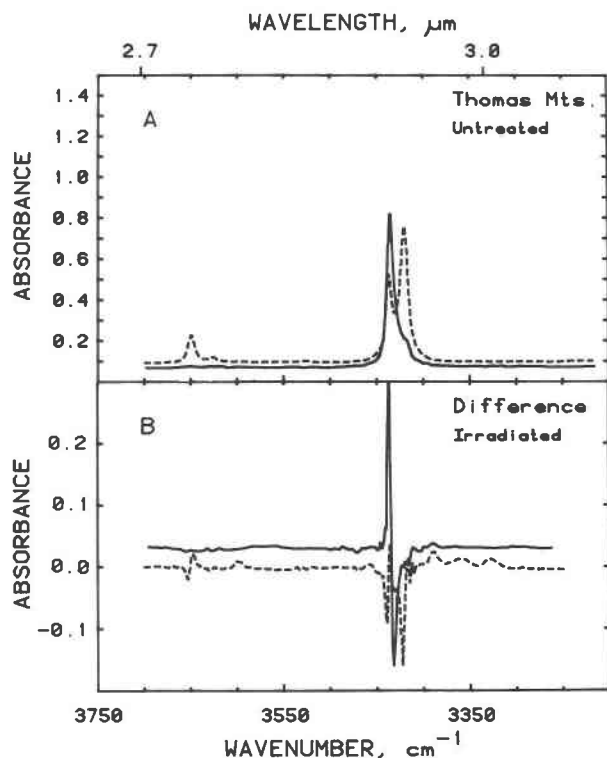


Fig. 7. (A) IR of naturally brown topaz from Thomas Mountains shown also in Fig. 6. The anticipated peak at  $3650\text{ cm}^{-1}$  is dominated by the peaks at  $3400\text{--}3450\text{ cm}^{-1}$  caused by anomalous OH species. Sample thickness  $1.37\text{ mm}$ . Solid trace— $\beta$  polarization; dotted trace— $\alpha$  polarization. Run at  $307\text{ K}$ . (B) The difference spectrum (irradiated sample minus initial sample) showing a decrease in most of the  $3400\text{--}3500\text{ cm}^{-1}$  absorptions which is associated with the formation of the brown color.

The  $460\text{-nm}$  brown-producing absorptions are seen as in the Thomas Mountains samples, and an additional absorption resulting in the blue color is seen at  $640\text{ nm}$ . The differences in the optical region are accompanied by differences in the IR region. Although both the brown and blue zones contain a large number of anomalous IR absorptions, they are more intense in the brown zone and are dominated by absorptions in the  $3400\text{--}3450\text{ cm}^{-1}$  region as in the Thomas Mountains samples. (The IR spectrum of the lighter-brown zone is intermediate in behavior to the two shown).

Two methods were used to bleach portions of this sample: exposure to direct sunlight for 4 h and heating at  $240^\circ\text{C}$  for 10 min. The sunlight bleaching only affected the  $460\text{-nm}$  peak (Fig. 9) and had no effect on the IR spectrum of any of the color zones. The effect on the  $460\text{-nm}$  peak was the same in all color zones.

Heating the sample for 10 min at  $250^\circ\text{C}$  resulted in dramatic changes in both the visible and IR spectra. All traces of brown disappeared. Figure 10 shows the changes in the IR region after heating (i.e., spectrum of heated sample minus that of unheated sample). The effects in the  $3300\text{--}3450\text{ cm}^{-1}$  region are the opposite of those seen in

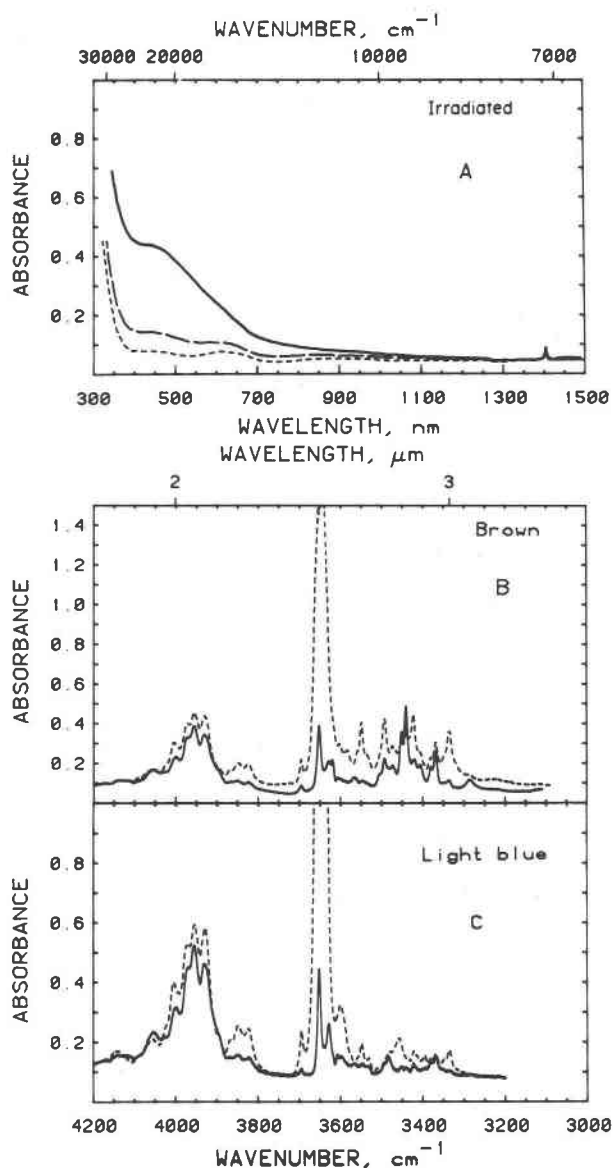


Fig. 8. (A) VIS-NIR spectra of Brazilian topaz irradiated with electrons. Three color zones exist: solid trace—brown; long dashed trace—light brown; short dashed trace—light blue. Sample thickness  $1.0\text{ mm}$ ,  $\alpha$  polarized. (B) IR spectra of the brown zone at  $77\text{ K}$ . Solid trace— $\beta$  polarization; dashed trace— $\alpha$  polarization. (C) Light-blue area, under the same conditions.

the Thomas Mountains sample after irradiation, as might be expected. There is also increased absorption in the  $3500\text{-cm}^{-1}$  region, where no absorptions occur in the Thomas Mountains samples. Figure 11 compares the changes in the three color zones. There is a definite correlation between the intensity of the IR changes and those in the VIS-NIR region.

It appears that the only radiation-damage center associated with the anomalous hydrous components is the more stable brown color caused by the absorption tail from the UV region. Neither the blue color nor the less

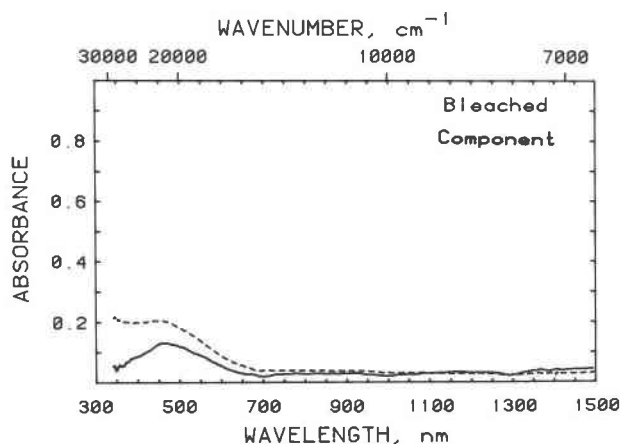


Fig. 9. The component bleached from the brown zone of the sample in Fig. 8 by 4 h of direct sunlight (difference spectrum, untreated minus bleached). Solid trace— $\beta$  polarization; dashed trace— $\alpha$  polarization.

stable (sun-bleachable) brown component resulting from the absorption at 460 nm is associated with a hydrous species. Dickinson and Moore (1967) correlated an ESR active center with a yellow-brown radiation-produced color in topaz. They assigned this hole center to an  $O^-$  attached to Si, surrounded by 6  $F^-$  ions. Which of the two brown colors observed in this study might represent their yellow-brown color is unclear, since they presented no optical spectra. However, this is a very similar kind of hole center to that causing the smoky color in quartz, in which both an electron and proton diffuse away from the hole center. This could be the mechanism responsible for the coupling of radiation damage to the hydrous component in topaz; an  $(OH^-, F^-)$  site containing  $F^-$  could not form such a hole center.

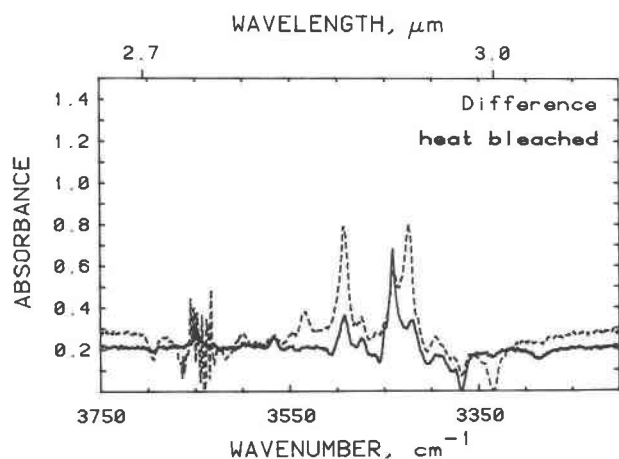


Fig. 10. Changes in the IR spectrum of the electron-irradiated Brazilian topaz (brown zone) brought on by heating for 10 min at 250°C. Spectrum of heated sample minus that of unheated sample (positive deviations represent an increase in intensity during bleaching). Obtained at 77 K. Solid trace— $\beta$  polarization; dashed trace— $\alpha$  polarization. Sample thickness 1.0 mm.

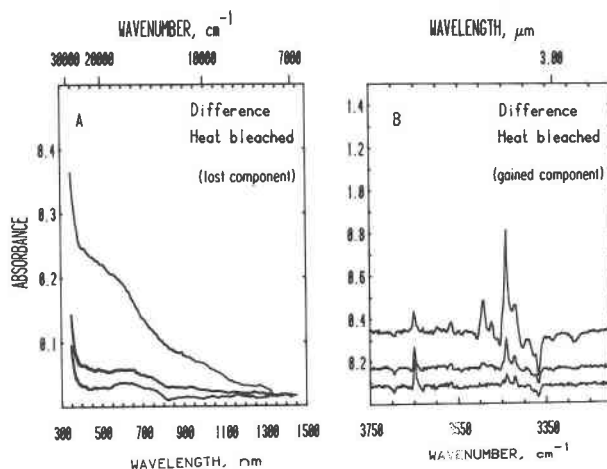


Fig. 11. Comparison of changes in the VIS-NIR (A) region with those in the IR (B) after heating of electron-irradiated topaz. VIS-NIR difference is unbleached minus bleached, the opposite of the IR. Upper trace—brown zone; middle trace—light-brown zone; lower trace—light-blue zone. Both IR and VIS-NIR spectra are  $\beta$  polarized, sample thickness 1.0 mm. IR spectra obtained at 77 K; VIS-NIR at 300 K.

The anomalous nature of the participating hydrous component suggests that there is an additional hydroxyl site. One such site is suggested by the work of Parise et al. (1980). They suggested that normally two hydroxyl groups cannot occupy adjacent sites because the protons approach too closely. If adjacent sites were occupied, however, the protons would be deflected to new positions, lowering the symmetry of the crystal. This is one possible anomalous H site in topaz; others are certainly possible. For example, the types of defects found in quartz (Kats, 1962) may occur. We cannot at this time assign the radiation-active proton species to a specific site in the topaz structure.

## CONCLUSIONS

The presence of a hydrous component can apparently hinder the formation of smoky quartz and amethyst or help in the formation of amazonite, metamict zircon, and colors in topaz when these minerals are subjected to irradiation. It is now possible to identify some actual mechanisms that involve the hydrous component. They indicate that the mobility and reactivity of H species in silicates are responsible for the relationship between radiation damage and hydrous species. In the cases discussed here, H species are involved in annealing charge imbalances, and as such are hindering total radiation damage despite the possibility that a new color may result from this process. The mobility of protons and atomic H at room temperature make it possible for a small amount of a hydrous component to control the radiation behavior of a crystal. This, coupled with the large number of possible H species, makes H a unique participant in the radiation-damage process.

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