Role of natural radiation in tourmaline coloration

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Abstract

The optical spectra of elbaite tourmalines subjected to large, controlled doses of gamma radiation have been compared to those of natural specimens. Both naturally pink and laboratory-irradiated elbaites show the same spectroscopic features. Optical absorption features of Mn^{2+} in nearly colorless elbaites are lost during laboratory irradiation, indicating a $Mn^{2+} \rightarrow Mn^{3+}$ transformation during the radiation process. Measurements of the radiation levels in tourmaline pockets in southern California pegmatites have been used to compute the doses that natural samples should have experienced over geologic time. These doses generally correspond to the doses required to restore the color to elbaites that have been decolorized by laboratory heat treatment, indicating that color in naturally pink tourmaline is a product of natural radiation. This radiation could have been effective only after the pegmatite cooled below the decolorizing temperature of tourmaline, suggesting that most pink elbaites originally grew nearly colorless in the pegmatites and only later attained their pink color through oxidation of Mn via ionizing radiation.

Introduction

High-energy ionizing radiation is capable of changing the color of several minerals and inducing a variety of radiation-damage centers that include trapped electrons and oxidized or reduced cations and anions. The detailed atomic processes accompanying these changes are often poorly understood. It has long been recognized that many minerals change color when they are irradiated in the laboratory. The new colors that develop frequently resemble the colors of naturally occurring varieties of the mineral. Furthermore, the natural color of many minerals can be cyclically removed by heating and restored by irradiation. Therefore, it is often stated that the colors induced by laboratory irradiation are identical to natural colors with the tacit assumption that the underlying atomic-level color origins are also identical.

There are few quantitative studies that have examined these concepts in detail. Two questions need to be addressed: what are the detailed transformations that occur when a mineral is irradiated, and do the changes induced in the laboratory correspond to those that occur in nature? These questions can be answered in part from a comparison of the spectroscopic data from natural and laboratory-irradiated minerals. It is possible that the answer will be different for different minerals. It is also necessary to estimate the radiation doses experienced by minerals in nature in order to determine whether the radiation doses applied to laboratory samples are similar to those that a mineral experiences in its natural setting.

In this paper we consider the coloration of pink elbaite. Bershov et al. (1969), Nassau (1975), and others have

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observed that both gamma and X-radiation develop and intensify pink color in elbaites and that heat treatment at 600 °C removes both the natural and irradiation-induced color. A variety of studies have presented the visible and near-infrared spectra of pink tourmalines and proposed explanations for the colors (Bershov et al., 1969; Wilkins et al., 1969; Manning, 1969, 1973; Bakhtin et al., 1975), but have not dealt with the role of radiation. In particular, none of these studies address the issue of whether laboratory irradiation duplicates or even approximates natural processes in detail.

Experimental details

Absorption spectra were taken using procedures described in Rossman (1975). Samples (Table 1) were chosen to represent a variety of localities. Irradiations were performed in a 190-Curie ^{137}Cs source at a rate of 1.4 Mrad/d of 0.66 MeV gamma rays. Heating experiments were performed in air.

Results and discussion

Dose considerations

To consider the role of natural radiation in tourmaline coloration, two approaches were used. The first was to calculate the theoretical dose a crystal should receive from the host minerals of a typical pegmatite. The second involved actually measuring the radiation level in tourmaline pockets.

The theoretical dose was calculated using Jahns's (1954) description of a typical southern California granitic pegmatite. The crystal was modeled as a sphere 1.8 cm in radius in the center of a 1.0-m radius sphere of composition 60 mol% potassium feldspar, 30% quartz, and 10% albite. Because the pink tourmaline crystals are often in part surrounded by quartz, the calculation was concerned
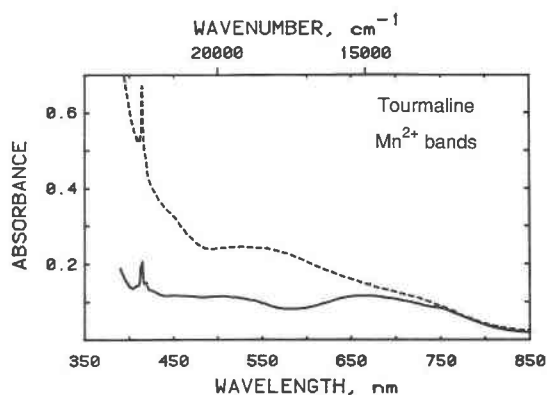
Fig. 1. Optical absorption spectrum of nearly colorless, high-Mn elbaite (807) from the San Diego mine, which shows Mn^{2+} features. Polarizations: solid line: $\mathbf{E} \| \mathbf{c}$; dashed line: $\mathbf{E} \perp \mathbf{c}$. Sample 7.06 mm thick.

Fig. 2. Beer's law plot for the Mn^{2+} bands at 414 nm, $\mathbf{E} \perp \mathbf{c}$ (diamond); 412 nm, $\mathbf{E} \| \mathbf{c}$ (cross); and 414 nm, $\mathbf{E} \| \mathbf{c}$ (rectangle). A linear fit to the first two is indicated.

only with ^{40}K gamma radiation that is capable of penetrating to the interior of the pocket. From the mass attenuation coefficients for gamma rays (Davisson and Evans, 1952) the half-path length of the 1.5-MeV ^{40}K gamma ray through the idealized pegmatite is 5.25 cm. Under the simplifying assumption that the mass density of ^{40}K is constant throughout the granite, the calculation indicates that the mineral receives a dose of 30 Mrad over 100 m.y., the approximate age of pegmatites in the Mesa Grande district (Foord, 1976).

To compare these estimates with the radiation level actually encountered in a pegmatite, a calibrated Geiger counter probe was placed in four tourmaline gem-pockets in the Himalaya mine, Mesa Grande, California, as they were being mined, and in an emptied pocket in the Maple Lode mine, Aguanga Mountain, California. In all cases these measurements indicated that doses of the order of 35 to 45 Mrad would be accumulated over 100 m.y.

Oxidation states of Mn in elbaite

The oxidation states of Mn in tourmaline must be determined before the details of the radiation-induced changes can be discussed. Several authors have associated the color of natural pink elbaites with Mn^{3+} (Manning, 1973), but no one has identified Mn^{2+} features in their optical absorption spectra. The spectroscopic features of Mn^{2+} should be easily recognized by their narrow, weak absorption bands between 410 and 420 nm (Keester and White, 1966). Because previous spectroscopic studies have been concerned with pink to red tourmalines, we examined a nearly colorless, Mn-rich core of an elbaite (sample 807) from the San Diego mine (Foord, 1976). Its spectrum shows the weak, spin-forbidden Mn^{2+} absorption bands at 414 nm in the $\mathbf{E} \perp \mathbf{c}$ polarization and at 419, 414, 412, and 408 nm in the $\mathbf{E} \| \mathbf{c}$ polarization plus other broad features that are due to the combined features of Mn and the other minor constituents (Fig. 1). The spectra of other naturally colorless samples or samples rendered colorless by heat treatments show the same Mn^{2+} fea-
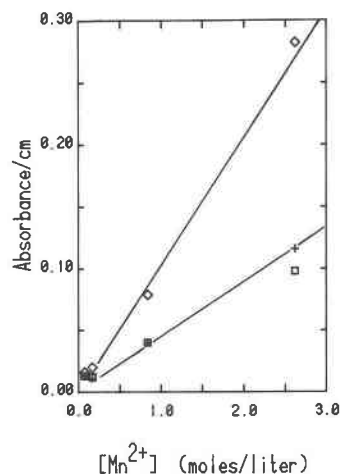
tures, as did the yellow-green, high-Mn^{2+} Zambian elbaites discussed by Rossman and Mattson (1986) and Shigley et al. (1986).

A Beer's law plot (absorbance at 414 nm vs. Mn concentration) of a number of samples rendered colorless by heat treatment yields the molar absorptivity (ϵ value) of Mn^{2+} in elbaite of 0.10 ± 0.01 L/(mol·cm) for $\mathbf{E} \perp \mathbf{c}$ and $\epsilon = 0.044 \pm 0.004$ $\mathbf{E} \| \mathbf{c}$ (Fig. 2).

Response to irradiation

The intensities of the Mn^{2+} peaks decrease when the sample is irradiated. The heights of the peaks fall off roughly exponentially with increasing dose. Simultaneously, new bands appear and grow with increasing dose (Fig. 3). They are at 480 and 700 nm for $\mathbf{E} \| \mathbf{c}$ and at 390, 515, and 700 nm for $\mathbf{E} \perp \mathbf{c}$ (Fig. 4). In some samples the 390-nm band is obscured by an intense ultraviolet absorption. The 700-nm band grows on top of any pre-existing Fe^{2+} bands in the 700-nm region (Smith, 1978) that may be present in the heat-bleached crystals. These same bands are observed in naturally pink elbaites. These results demonstrate that Mn^{2+} initially present in the crystal is lost during the course of irradiation. The post-

TABLE 1. Localities and minor-element concentrations (in wt%)

Sample	Locality	MnO	FeO	CaO	TiO$_2$
565-A	Himalaya mine, Mesa Grande, California	1.19	0.02	0.60	0.03
565-B	Himalaya mine, Mesa Grande, California	0.24	0.08	0.34	0.01
595-A	Northeastern Afghanistan	0.69	0.73	0.54	0.06
614-S4	Stewart mine, Pala, California	0.39	0.11	0.15	0.01
743	Mozambique	0.28	0.07	0.28	0.01
745	Madagascar	0.17	0.07	0.06	0.01
807*	San Diego mine, Mesa Grande, California	3.57	0.03	1.08	0.02
808-A	Minas Gerais, Brazil	0.24	0.09	0.29	0.01

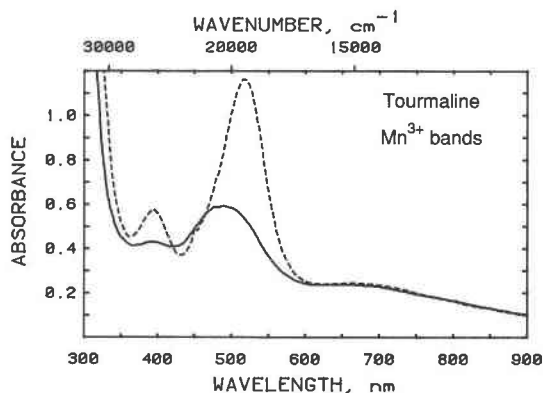* Analysis from Rossman and Mattson (1986).

Fig. 3. Optical absorption spectrum of elbaite (614-S4) from the Himalaya mine, 3.64 mm thick, first heated to 600 °C to decolorize it, then irradiated with 32 Mrad to turn it red. Solid line: $E \| c$; dashed line: $E \perp c$. Mn^{2+} bands at 414 nm are not observed after irradiation.

Fig. 4. Saturation curves for sample 565-A; optical absorbance vs. dose: squares, 515 nm (ω); cross, 480 nm (ϵ); diamond, 390 nm (ω).

irradiation oxidation state of the Mn that is responsible for the color of pink elbaites has previously been assigned by Manning (1973) and others to Mn^{3+}. Our results support this assignment. The fate of the electron that is driven from the Mn^{2+} is not established.

Concentration of Mn^{3+}

To determine the amount of Mn^{3+} that forms in pink tourmaline, we must calibrate the intensity of the Mn^{3+} absorption bands to derive the molar absorptivity of Mn^{3+}. The molar absorptivity was estimated from experiments where elbaites were subjected to a series of moderate doses of radiation. The decrease in Mn^{2+}-band intensity and the growth of Mn^{3+} bands were measured under the assumption that all the Mn^{2+} lost was converted to Mn^{3+}. This experiment was done most readily with the sample 807 from the San Diego mine because of its high Mn^{2+} concentration. This sample was stepwise irradiated to 79.8 Mrad. Although the sample had not reached saturation at this point, the 414-nm band ($E \perp c$) decreased in intensity by 24.3%. Assuming that 24.3% of the Mn^{2+} had been oxidized in the irradiation, the following ϵ values were computed for Mn^{3+}: $\epsilon = 7.5$ at 515 nm for $E \perp c$; $\epsilon = 1.9$ at 480 nm for $E \| c$.

THE RADIATION CYCLE

The cycle of oxidizing Mn^{2+} in elbaite with gamma rays to yield a deep pink or reddish color and reducing the Mn^{3+} with heat treatments to remove the color is reversible. All of the samples used in this study were brought through the full cycle at least once. The ease with which the color is lost at moderate temperatures in the laboratory indicates that the color could not have survived under the temperature of crystallization. The fluid-inclusion and phase-stability studies of London (1986) indicate that the tourmalines in the southern California pegmatites crystallized at about 450 °C. The isotopic and fluid-inclusion studies of Taylor et al. (1979) indicate that
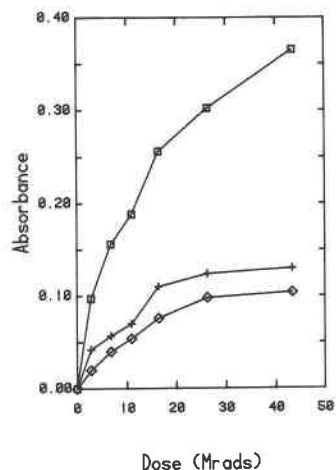
the tourmaline pockets formed over the range of 565 to 525 °C. Our bleaching experiments on sample 565 show that the color is rapidly lost at 600 °C and that partial bleaching occurs in 5 d at 500 °C. Sample 614 showed partial bleaching after 6 h at 250 °C. Our conclusion is that the pink color in these elbaites could not have existed at the temperature of crystallization but rather developed postcrystallization under the influence of external radiation at a lower temperature.

Comparison of natural and laboratory-irradiated elbaites

Elbaites from a variety of localities were examined both in the natural state and after heat treatment and/or laboratory irradiation to determine whether all elbaites displayed identical spectroscopic behavior. These results show that bands in the visible region of the optical spectrum occur in the same positions for all samples. Some variation was observed in the ultraviolet region, but it appears to be related to the Fe content of the samples. Thus, we conclude that irradiation causes the oxidation of Mn^{2+} to Mn^{3+} in all elbaites and that laboratory irradiation duplicates the natural process.

Added support for the natural irradiation origin of the color of pink tourmaline comes from irradiation experiments. A portion of the Himalaya mine sample was first decolorized at 600 °C and irradiated with 30 Mrad, the calculated level of natural exposures. The resulting depth of color in the irradiated crystal was essentially visually identical to a control sample that had been left in its natural state.

Problems remaining

Some elbaites from pegmatite districts are pale pink to nearly colorless but contain Mn and readily develop deep pink colors upon exposure to gamma radiation in the laboratory. Sample 807 is a case in point. In our experi-

ence, these examples are relatively few in number. Their existence does not contradict the conclusions developed above. Nassau (1975) has previously noted that after laboratory irradiation, some tourmalines that develop red colors are susceptible to fading after several weeks of exposure to sunlight and that there is a range of stability to elevated temperatures. These observations indicate that not all electron-receptor sites in tourmaline have the same stability. Consequentially, even though all tourmalines in a given pegmatite are exposed to natural levels of radiation and are experiencing the radiation-induced transition of Mn^{2+} to Mn^{3+}, some will be unable to maintain an accumulation of Mn^{3+} because of the intrinsic instability of the electron receptors. The identity and nature of these receptors are not yet known.

CONCLUSIONS

Pink color in elbaite from a variety of pegmatite localities is the result of natural radiation. When these tourmalines originally grew, they contained Mn^{2+} and were very pale colored. Over geologic time, exposure to background levels of gamma radiation from ^{40}K caused the gradual formation of Mn^{3+}, which is responsible for the pink to red colors that the crystals now possess. In some pale-colored elbaites this process has not gone to completion so that it is often possible to oxidize the remaining Mn^{2+} to Mn^{3+} by laboratory irradiation, duplicating the natural irradiation process and producing results that are spectroscopically identical to the natural crystals.

REFERENCES CITED

Bakhtin, A.I., Minko, O.Y., and Vinokurov, V.M. (1975) Isomorphism and colour of tourmaline. Izvestiia Akademii Nauk SSSR, Geologic Series, 6, 73–83 (in Russian).

Bershov, L.V., Martirosyan, V.O., Marfunin, A.S., Platonov, A.N., and Tarashehan, A.N. (1969) Color centers in lithium tourmaline (elbaite). Soviet Physics–Crystallography, 13, 629–630.

Davisson, C.M., and Evans, R.D. (1952) Gamma-ray absorption coefficients. Reviews of Modern Physics, 24, 79–107.

Foord, E.E. (1976) Mineralogy and petrogenesis of layered pegmatite-aplite dikes in the Mesa Grande district, San Diego County, California, p. 123–177. Ph.D. thesis, Stanford University, Stanford, California.

Jahns, R.H. (1954) Pegmatites of southern California. California Division of Mines and Geology Bulletin 170, chapter 7.

Keester, K.L., and White, W.B. (1966) Crystal-field spectra and chemical bonding in manganese minerals. Proceedings, 5th International Mineralogical Association Meeting, Cambridge, England, 22–35.

London, David. (1986) Formation of tourmaline-rich gem pockets in miarolitic pegmatites. American Mineralogist, 71, 396–405.

Manning, P.G. (1969) An optical absorption study of the origin of colour and pleochroism in pink and brown tourmalines. Canadian Mineralogist, 9, 678–690.

——(1973) Effect of second-nearest-neighbor interaction on Mn^{3+} absorption in pink and black tourmaline. Canadian Mineralogist, 11, 971–977.

Nassau, K. (1975) Gamma-ray irradiation induced color changes in the color of tourmaline. American Mineralogist, 60, 710–713.

Rossman, G.R. (1975) Spectroscopic and magnetic studies of ferric iron hydroxy sulfates: Intensification of color in ferric iron clusters bridged by a single hydroxide ion. American Mineralogist, 60, 698–704.

Rossman, G.R., and Mattson, S.M. (1986) Yellow, Mn-rich elbaite with Mn-Ti intervalence charge transfer. American Mineralogist, 71, 599–602.

Shigley, J.E., Kane, R.E., and Manson, D.V. (1986) A notable, Mn-rich gem elbaite tourmaline and its relationship to "tsilaisite." American Mineralogist, 71, 1214–1216.

Smith, G. (1978) A reassessment of the role of iron in the 5,000–30,000 cm^{-1} region of the electronic absorption spectra of tourmaline. Physics and Chemistry of Minerals, 3, 343–373.

Taylor, B.E., Foord, E.E., and Friedrichsen, H. (1979) Stable isotope and fluid inclusion studies of gem-bearing granitic pegmatite-aplite dikes, San Diego County, California. Contributions to Mineralogy and Petrology, 68, 187–205.

Wilkins, R.W.T., Farrell, E.F., and Naiman, C.S. (1969) The crystal field spectra and dichroism of tourmaline. Journal of Physics and Chemistry of Solids, 30, 43–56.