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BLACKENING OF NATURAL QUARTZ BY γ-IRRADIATION

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INTRODUCTION

Numerous studies of color centers in natural and synthetic quartz have been made in recent years, and the general relationship of color centers in smoky quartz to chemical substitution and γ-irradiation has been established by a number of investigators: Griffiths, Owen and Ward (1954), O'Brien (1955), Cohen and Sumner (1958), Cohen (1956, 1960), Bambauer (1961), Bambauer, *et al.* (1960), and Kats (1961). The mechanism of color center development as proposed by O'Brien (1955) whereby interstitial ions are neutralized by γ-radiation is generally accepted.

Hayase (1961) qualitatively (visibly) studied the effect of gamma irradiation on natural quartz. He found that natural smoky quartz could be decolored by heating it at 600° C. for five minutes. His samples were then irradiated by using a 2000 Curie cobalt 60 γ-ray source. Quartz from extrusive igneous rocks, formed at relatively high temperature, were darkened to a greater degree than quartz from granite and from low temperature hydrothermal veins. Quartz from gneissic and crystalline schistose rocks was relatively little effected. Hayase found a correlation between natural radioactivity and the degree of smokiness of quartz from granite. He states that the quartz in granites containing a high radium content ($2-3\times10^{-12}$ g/g, *i.e.* 10 grams per ton uranium) was considerably smoky, whereas that from weakly radioactive granite (under 10^{-12} g/g radium) shows no appreciable smokiness.

Keith and Tuttle (1952) found that, in general, the inversion temperature of quartz is inversely proportional to the amount of impurity atoms present, and to the temperature of formation of the quartz. They suggest that the inversion probably starts around centers of local strain, such as might be found around impurity atoms, which "trigger" the inversion. They propose that the inversion temperature can be used as an indication of the relative temperature of formation of samples of quartz which have grown in similar chemical environments, but not as an indication of temperature of formation of rocks of widely different chemical composition.

Bambauer (1961) measured the H, Li, Na and Al content of a large number of vein quartz samples from the Swiss Alps and, after careful correlation of impurity content with amount of blackening, he concludes that the color centers are formed by Li–Al defects and that H-Al and Na-Al defects are probably not potential color centers.

EXPERIMENTAL DATA AND RESULTS

Samples for this study were polished rock slices .020 ± .002 inches thick which were irradiated in 15 minute increments using a Norelco *x*-ray fluorescence unit having a tungsten target FA-60 tube operated at 50 kilovolts and 40 milliamperes. Light transmission before and during the blackening runs was measured with a Hilger non-recording microphotometer. Irradiation was continued until saturation blackening was attained, a period varying from 15 to 90 minutes. No corrections for optical orientation of the quartz were applied. The results are expressed as "per cent of blackening"—per cent of difference of intensity of light transmitted through irradiated and unirradiated quartz (Fig. 1).

The constancy of reaction of quartz to repeated bleaching and heating, and the order of magnitude of natural blackening that some quartz can attain was demonstrated by the following experiment: A randomly oriented slice was cut from naturally smoky pegmatite #10, which was visibly very dark (see appendix). The slice was then broken into specimens A and B. Specimen A was irradiated and measured in the usual manner. Specimen B was heated at 400° C. for two ten minute periods. All visible smokiness disappeared and the specimen was 22.1% lighter than it had been before heating. It should be noted here that several darkened quartz samples were heated at temperatures above the inversion temperature of approximately 573° C. Although they appeared to be lighter in color, they were photometrically more opaque after heating than before. Perhaps minute fracturing or inversion twinning took place when the quartz was taken over and then brought back through the inversion temperature. Darkened quartz can be adequately bleached by heating it to 400° C. for ten minutes.

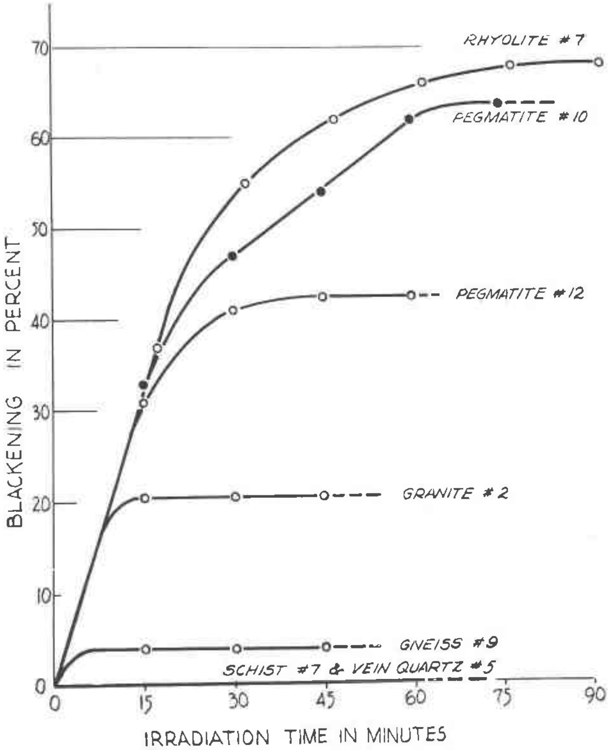

FIG. 1. Representative blackening curves.

Specimen B was irradiated, measured, and its blackening curve plotted. This curve has the same shape as that for specimen A, but it is displaced upward by about 12% of blackening. Both specimens were bleached and reirradiated. They both followed the same upper curve that specimen B had followed the first time it was irradiated. Figure 2 is a "hysteresis-type" plot of the data.

The possibility that growth or sector zoning might be an uncontrolled variable in a study of quartz blackening was examined by Ritter and

Dennen (1964) who concluded that zoning is very rare in the quartz of primary igneous rocks. Hayase (1961) concurs when he states, "a large crystal of pegmatitic quartz very often shows a zonal structure of various smokiness grades, but the granitic samples are never heterogeneous in smokiness."

In the present study, 122 specimens of quartz from 58 rock samples comprising seven types of natural quartz—granitic, rhyolitic, pegmatitic, gneissic, schistose, and vein quartz and one synthetic quartz specimen were examined (see appendix). Only one sample of visibly smoky quartz was used, so it was deemed not necessary to heat-bleach the specimens before irradiating to put the samples on a common level of blackness.

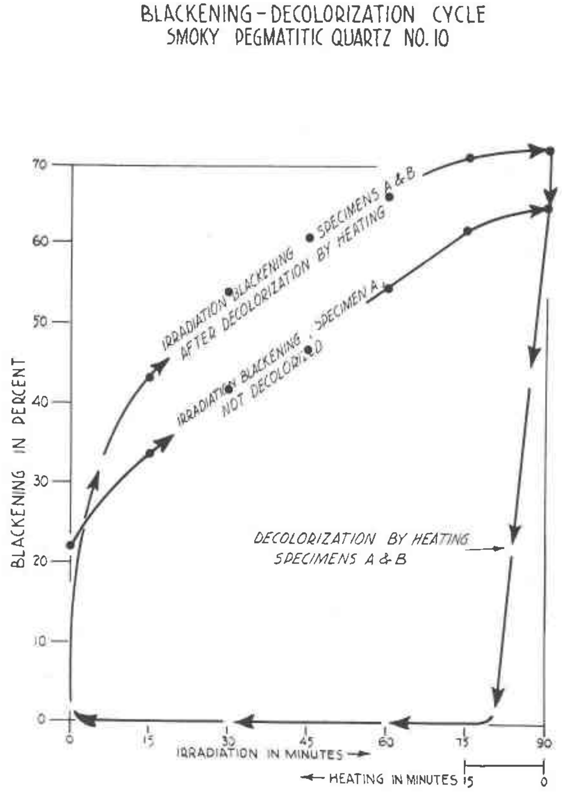

FIG. 2. "Hysteresis-type" blackening-decoloration curves.

The data obtained from the study of granitic and rhyolitic quartz samples may be epitomized as follows: (1) five out of seven rhyolitic quartz samples show saturation blackening of over 45%; (2) only two out of 11 granitic quartz samples showed blackening over 45% and eight of the granitic quartz samples fall below 25%; (3) the greatest blackening at saturation attained by any of the quartz samples examined was 73% for rhyolitic quartz #12. All of the granitic quartz samples showed, essentially, the same shape of curve with the saturation value usually being reached at the end of 30 minutes of irradiation. The rhyolitic quartz curves are quite similar to those for granitic quartz, but are displaced upward.

Two differently shaped curves were found for pegmatitic quartz. Four of the ten pegmatitic quartz samples examined have blackening curves similar to those for granitic quartz. The other samples, however, blackened along a characteristically shaped compound curve which was not shown by any other type of quartz. Unfortunately the exact geologic setting of these samples is not known, and no correlation can be made between curve shape and type of pegmatitic quartz, *i.e.* from simple or complex pegmatites or from specific zones within a complex pegmatite.

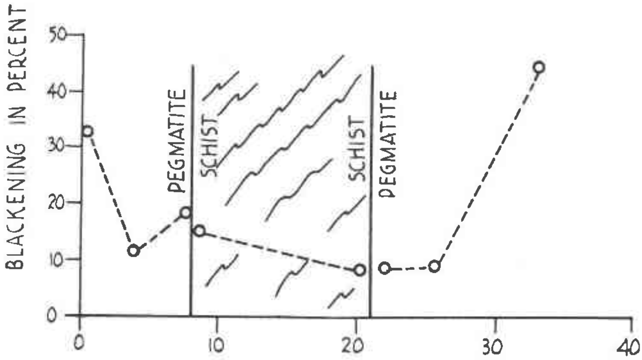

FIG. 3. Irradiation blackening of quartz in Pegmatite Dikes and Bolton schist, Strickland Qy., Conn.

Of the eight quartz samples from gneisses, only one (#10) showed blackening at saturation of over 6.5%. Of the five schistose quartz samples, four developed no blackening at all. The one sample that did (#5) came from a kyanite schist (high temperature of formation). Of the eight samples of vein quartz examined, only one (#4) showed any blackening. Figure 1 shows representative curves for different quartz types.

Eight samples of pegmatitic quartz (#12) were taken across contacts between pegmatite dikes and schist in the Strickland Quarry, Connecticut (Fig. 3). The amount of blackening in the quartz taken near the contacts was much less than that of samples obtained at some distance from the contacts. Blackening in the quartz of the schist was low.

Discussion

Bambauer (1961) demonstrated that color centers in quartz are related to Li-Al defects but not to H-Al or Na-Al defects. The Al content of some of the present samples has been measured spectrographically following the procedure described by Dennen (1964) and the results plotted against per cent blackening in Fig. 4. The dashed line apparently represents the approximate relationship of blackening to the Li-Al defect (note the clustering of pegmatitic quartz) while the scatter of other points implies that other elements than Li are compensating for the charge deficiency arising from the proxy of Al^{3+} for Si^{4+}.

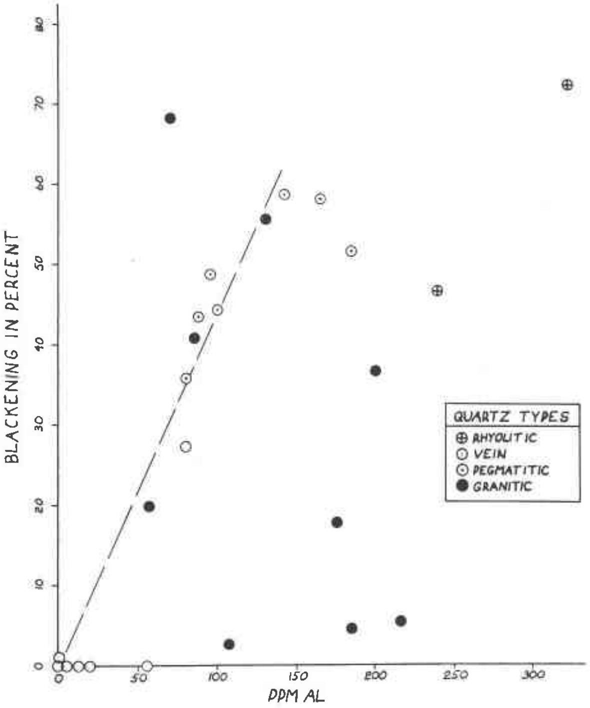

FIG. 4. Plot of blackening in per cent versus trace aluminum content.

The different blackening at saturation of different types of natural quartz shows a rough relationship between temperature of formation and amount of impurity atoms. The strong blackening attained by rhyolitic quartz, the intermediate darkening attained by granitic quartz, and the low or nil smokiness developed in metamorphic and hydrothermal vein quartz are the same relative "smokiness grades" which Hayase (1961) found. The variation in blackening of the pegmatitic and wall-rock quartz (#12) from the Strickland Quarry, Connecticut (Fig. 3) could thus be a reflection of the temperatures attained in this system.

A comparison of our results with those of Keith and Tuttle (1952) shows that rhyolitic quartz, which attains a high degree of radiation blackening, has a relatively low inversion temperature whereas vein quartz, which shows little or no blackening, has a relatively high inversion temperature. Also, they found that "the inversion temperatures of quartz from simple pegmatites fall into a comparatively narrow temperature range whereas the range of inversion temperatures of quartz from zoned pegmatites is nearly as great as that of all other types of quartz combined." It may be that the two kinds of blackening curves for pegmatitic quartz found in this work may represent these two kinds of pegmatites.

CONCLUSIONS

Natural quartz of different geologic origin is blackened to different degrees and at different rates by γ-irradiation. These differences can be detected and semiquantitatively measured.

Broad differences between the blackening of quartz from different environments may be of value in studies of provenance and the detailed differences between the quartz of similar environments may serve for correlation as well.

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Appendix. Description and Geographic Location of Some of the Samples Used

Sample	Location	% Blackening at Saturation	ppm Al
I. *Granitic Quartz*			
No. 2—Granodiorite	Lincoln, Placer Co., Calif.	18	
4—Granite	Rocklin, Calif.	37	84
5—Porphyritic granite	Southern slope of Pike's Peak, Colo.	56	125
7—Grey granite	Aberdeen, Gunnison Co., Colo.	3.5	
8—Granite	Summit of Pike's Peak, Colo.	65	
9—Biotite granite	Ute Pass, Hamilton, Colo.	20	56
11—Granite porphyry	Frotet Lake Area, Chibougamau, P. Q., Canada	4	185
13—Granite	(Quincy Granite) Quincy, Mass.	22	
14—Red granite	Frotet Lake Area, Chibougamau, P. Q., Canada	5.5	215
16—Granite	Llano, Texas	2.5	
17—Aplite	Peabody Granite Batholith, Lawrence, Mass.	6.5	
II. *Pegmatitic Quartz*			
*No. 1—Smoky Quartz	New England	58	165
4—Tourmaline pegmatite	Mt. Apatite, Maine	59	142
* 5—Quartz-feldspar peg.	South Glastonbury, Conn.	49.5	94
6—Tourmaline pegmatite	Mt. Rubellite, Maine	43	87
* 9—Graphic granite	Hale Quarry, Conn.	44	100
11—Garnet-bearing pegmatite intruding gneiss	Harvard, Mass.	36	80
* 10—Smoky Quartz	New England	65	
12—Tourmaline peg.	Strickland Quarry, Conn.	45	
* Compound blackening curve (see Fig. 1)			
III. *Vein Quartz*			
No. 1—Vein quartz in greenstone	Chibougamau, P. Q., Canada	0	
2—Vein quartz in meta-volcanics	Chibougamau, P. Q., Canada	0	0
3—Vein in schist	Montpelier, Vt.	28	80
4—Vein (with graphite) in schist	Johnsonburgh, N. Y.	0	
6—Vein in slate	Lyndon, Vt.	0	1
7—Vein quartz	Squantum, Mass.	0	6
8—Vein (with wolframite)	Unknown	0	
IV. *Schistose Quartz*			
No. 1—Quartz-hornblende schist	Chipman Mine, Mass.	0	
4—Chrome mica schist	Unknown	0	
5—Kyanite schist	New England	28	
6—Manhattan schist	New York, N. Y.	0	
7—Chlorite muscovite schist	New England	0	
V. *Gneissic Quartz*			
No. 3—Gneissic granite	Bedford, Mass.	5	
5—Biotite gneiss	Lincoln, Mass.	0	
6—Migamite	Guiges Lake Area, Chibougamau, P. Q., Canada	4	
7—Quartz muscovite schist	New England	0	
8—Para-gneiss (contains garnet)	Lake Muskoka, Gravenhurst, Ont., Canada	1	
9—Banded gneiss	New England	4	

APPENDIX—*(continued)*

Sample	Location	% Blackening at Saturation	ppm Al
10—Banded gneiss-bands of biotite mixed with quartz, feldspar, and muscovite	New England	21	
11—Gneiss-schist	New England	0	
VI. *Rhyolitic Quartz*			
No. 1—Rhyolite	Castle Rock, Colo.	58	
7—Light grey rhyolites with phenocrysts of quartz, hornblende, and feldspar	New England	68	
8—Rhyolite with phenocrysts of quartz and feldspar	Unknown	32	
10—Rhyolite porphyry	Spikarna, Alno, Sweden	48	250
12—Extrusive rhyolite	South Tyrol, Italy	73	320
13—Quartz porphyry	Meissen, Germany	57	

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WHEWELLITE FROM SEPTARIAN CONCRETIONS NEAR MILAN, OHIO

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About one mile west of Milan, Ohio, which is two miles south of Exit 7 on the Ohio Turnpike, the Huron River cuts through flat-lying beds of the marine Ohio and Olentangy shales of Upper Devonian age. Concretions one to three feet in diameter are quite common here and many are septarian. Three years ago Clarence Raver, an amateur rock hound from Clarksfield, Ohio, began breaking these open and collecting specimens of fluorescent calcite, dolomite, ankerite, barite, marcasite, quartz and sphalerite. He was unable to identify one colorless crystalline material, several pounds of which he found in more than 25 septarian concretions. Well crystallized samples about 3×2×1 in. were brought to our attention in October 1963 and have since been identified as whewellite, calcium oxalate monohydrate.

Powder *x*-ray diffraction data were in excellent agreement with those of Pecora and Kerr (1954) and Gude *et al.* (1960).

Chemical composition was similar to the theoretical for whewellite and to other analyses for this mineral from Europe. Table 1 contains the several analyses. Samples were also submitted for *x*-ray spectrographic examination and were found to be exceptionally pure.

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