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RADIATION COLORATION OF SILICA MINERALS*

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ABSTRACT

Radiation produced color centers in both natural and synthetic silicas are associated with impurity atoms although, since impure silicas do not always form color centers upon irradiation, these impurities *per se* are not sufficient to cause coloration. For trivalent impurities the extent and type of coloration seems to depend more upon the manner of incorporation rather than the identity of the impurity atom, although the identity will naturally affect the type of center formed. The degree of general disorder may be important, but specific defects, especially hydroxyl ions associated with positive hole traps, should also be considered. The difference in behavior between some natural specimens and those prepared or treated in the laboratory makes it doubtful that some of these natural quartz specimens were originally colored by ionizing radiation.

INTRODUCTION

The possibility that the colors of some minerals might result from the effects of radiation from naturally occurring radioactive associates was first suggested over half a century ago (1) and has been the subject of several extensive investigations (2). Amethyst and smoky quartz in particular have received the greatest amount of attention. It is now well established that high-energy irradiation of most quartz specimens will produce a smoky discoloration, and that the rate of formation and depth of this color are dependent upon the pre-existence of certain defects in the solid.

We have recently observed that silica gel containing certain impurities, if well degassed, develops a color upon irradiation with cobalt-60 gamma rays or with *x*-rays (3, 4). The color depends on the kind of impurities present; aluminum gives rise to an amethyst color while iron produces a smoky appearance. At room temperature the color is bleached by the action of various gases (hydrogen, water, and ethylene, for example) and by ultra violet light. It seemed possible that the gross characteristics of the radiation-produced colors in silicate minerals were identical with those produced in these gels, particularly since silica gel might be the progenitor of many hydrothermal silicate minerals, and that the chemical characteristics of these color centers, which are more easily studied on the gels because of their high surface area, might aid in characterizing and identifying the color centers in minerals and synthetic silicates.

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Experimental

All irradiations were done in a 750-curie Co^{60} gamma source (5). The dose rate for water* in the center, measured by ferrous sulfate dosimetry (6), was about 6×10^{17} *e.v.g.*$^{-1}$, or about 10,000 R, min^{-1}. Most of the specimens were obtained through commercial channels, hence their sources could not always be accurately defined. The ultra violet light used for bleaching was supplied by a Hanovia 125-watt germicidal lamp, which emits the 2537 Å wave-length almost exclusively. In order to detect slight color changes on ultra violet irradiation, specimens were partially screened with aluminum foil before bleaching. Changes or irradiation were observed visually, comparison with a control being used where necessary.

Results

In general many minerals when irradiated seem to follow the pattern similar to that observed with silica gel. Brazilian agates and "Pecos River Diamonds" (ferruginous quartz) both known to contain iron impurity, turn smoky to black during overnight irradiation. Fused silica, prepared by fusing the previously described gels in an oxygen-gas flame, show the same color patterns as those evidenced by the gels, *i.e.*, smoky for iron impurity and amethyst for aluminum impurity. Certain Mexican or Brazilian banded agates are very resistant to coloration; several days in the radiation source was required to obtain a noticeable effect. The banding is accentuated inasmuch as the opaque portions remained white and the transparent sections turned smoky. Feldspars (North Carolina sunstone, Indian moonstone, and Amelia Court House amazonite) acquire a smoky cast, although this is difficult to see in an opaque material. We have confirmed that opals cannot be colored at all (7), even those high in iron (Mexican cherry opal, for example) probably due to their comparatively high water content. Olivine peridotes and natural obsidian glass ("Apache tears") are also unaffected.

The widest variety of radiation sensitivity occurs among specimens of crystalline quartz. Most samples of natural hydrothermal quartz are easily turned smoky by an overnight irradiation. However, two samples of Brazilian oscillator-grade quartz remained clear during one week in the radiation source while two others became only faintly citrine. Some light amethysts (South Carolina) were also unaffected by a week's irradiation, Darker amethysts (Mexican and Brazilian varieties) and smoky quartz (Brazil, Maine, and North Carolina) after decoloration by heat regain their natural color on irradiation. Rose quartz from several localities (Georgia, Brazil and Maine) and citrine quartz (Maine and Brazil) are easily blackened in a few hours.

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* The dose rate for silica would not be greatly different.

All of the previously described materials when colored by γ radiation are bleached by long exposure (65 hours) to ultra violet light unless, of course, they are opaque. It is interesting to compare this behavior with that of the naturally occurring colored minerals. Natural amethysts (those which are fairly dark and which will recolor upon irradiation) can be only partially bleached by ultra violet light. Very long (1 week) exposures are required.

Sections of many specimens of smoky quartz will show patterns of light and dark areas. Three smoky quartz specimens were examined to see how these patterns were affected by gamma irradiation and by ultra violet light. A sliced section of Brazilian smoky quartz was partially screened and exposed to ultra violet light for sixty-five hours. No bleaching or darkening was noted (Fig. 1-A). The sample was then γ irradiated for three hours, which caused considerable darkening and a reversal of the pattern (Fig. 1-B). The light parts became darker than the (originally) dark sections. The sample was then partially screened and bleached with ultra violet light for 16 hours (Fig. 1-C). The extra darkening produced by the irradiation is made less intense, but the reversed pattern is still the one obtained. Finally the sample was completely bleached by heating to 300° C., re-darkened by irradiation and again bleached with ultra violet light. The sample was examined at intervals to ascertain if the original dark-light pattern of the natural crystal is reobtained. This is never the case, the pattern is always the "reversed pattern" of the irradiated crystal. Hence it is difficult to reason that this crystal could have derived its original color from a sequence of events involving natural radioactivity and excitations similar to those obtained from ultra violet light. Contact photographs are shown in Fig. 2.

FIG. 1. Drawings showing effect of gamma irradiation and ultraviolet bleaching on a smoky quartz section.

The same series of experiments was performed on a piece of smoky quartz from Maine with somewhat different results. Again a pattern of light and dark areas was noted, but an overnight exposure to ultra violet

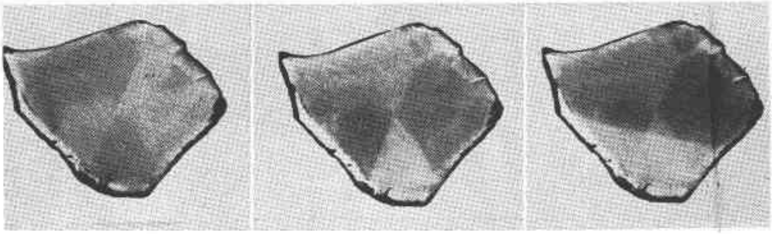

FIG. 2. Contact prints corresponding to Fig. 1.

light bleached the whole crystal section completely. Re-irradiation produced a general darkening but failed to reproduce the pattern. During bleaching with ultra violet light the pattern never reappears. Again it is difficult to imagine a sequence of naturally occurring events involving radioactivity as a coloring agent which would cause this type of behavior.

Finally we performed the same experiments on some smoky quartz, which is obviously colored naturally by irradiation, in order to determine if the effects of geological aging could result in this sort of behavior. The specimens of smoky quartz were collected by one of us (BMB) from the Pine Mountain Mine near Spruce Pine, North Carolina, where the quartz in the pegmatite occurs in association with torbernite (a copper uranium phosphate) as well as with the usual feldspar. The quartz in the undisturbed condition is darkest nearest the veins and crevices bearing the radioactive mineral, and gradually fades to white at a distance of one to three feet from the vein. Lightly colored and heat-decolorized pieces of Pine Mountain smoky quartz are easily darkened in the gamma source in three to five hours (1.8–3.0×10^6 R). The radiation level at uranium-bearing formations is generally from 1–5 R per year, and the local dosage immediately adjacent to a pocket or crystal of torbernite might be expected to be several times this value.* Hence, any piece of Pine Mountain quartz associated with torbernite for about one million years should have had the opportunity to become darkened. The granular condition of the original specimens and the presence of dark inclusions of biotite make the bleaching and patterning phenomena previously described difficult to observe and nearly impossible to photograph. The sample is bleached by ultra violet light, however, and the dark-light patterns existing before heat bleaching are reproduced by irradiation.

DISCUSSION

It is generally accepted (8, 9, 10) that irradiation-produced color in quartz and silica is due to the presence of defects associated with one or

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* Measurements here of the beta-gamma radiation from a sample of torbernite-bearing rock about 1½* across gave 12 m.r., hr^{-1}, equal to about 100 R yr^{-1}.

more trivalent impurities, present to the extent of a few tenths of a per cent at most, incorporated substitutionally as replacements for silicon in the silicon-oxygen network. Iron and aluminum are the most common trivalent impurities mentioned. The tendency has been to associate the amethyst color with radiation-produced defects involving the presence of iron (11), and to connect the smoky appearance similarly with the presence of aluminum (9, 10). This evidence is based largely on spectrographic or chemical analysis of the specimens studied. Such evidence is not completely conclusive however, for the only silicas so studied which do not contain both iron and aluminum are fused silicas which contain either aluminum alone, and which then become amethystine upon irradiation, or which contain neither, in which case they remain colorless upon irradiation. Specimens have also been found or prepared which contain iron, aluminum, or both, and which fail to color upon irradiation (9, 12). Some of the experiments previously cited are also at odds with the results of this study, *i.e.* that ferruginous silicas (agate, fused silica gel, and quartz) become smoky upon irradiation, whereas silicas containing only aluminum (gel and fused silica at least) become amethystine.

Previous investigators have reported the effect of various pretreatments on the irradiation coloration of fused silica. Yokota (8) states that fused silica of an unspecified purity after being heated in an atmosphere of silicon at 1400° C., develops a purple color* upon irradiation. Kats (9*a*) finds that such an experiment gives no coloration if Corning Fused silica, in which Al and presumably Fe are absent, is used as a source material. He also finds that Heraeus fused silica containing Al develops more coloration upon irradiation if first heated at 1250° C. in an oxygen atmosphere. One would normally expect heating in silicon to increase the number of oxygen vacancies, and heating in oxygen to decrease their number.

We have observed that in silica gels the amethyst color is bleached by electron donors, but not by acceptors (3). More recent experiments have shown that if the gels are preheated in oxygen or hydrogen at 400–600° C., allowed to cool, and then freed of excess gas, their tendency to color and to adsorb hydrogen with decoloration is unaffected. Irradiated gels will also adsorb oxygen without decoloration. One would normally expect such oxygen adsorption to annihilate oxygen vacancies. Since this seems to leave the coloration unaffected, one may tentatively assume that the oxygen vacancy is not important to the irradiation-produced purple color center.

There are several ways in which a trivalent atom may be incorporated

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* Specifically optical absorption at 5400 Å. Where the exact spectrum is not measured the terms "amethyst" and "amethystine" are used.

into a silica lattice. Trivalent impurities cannot be substituted for silicon without concomitant changes which preserve electrical neutrality. Although these impurity configurations have been described by others (9, 10), we will list the four principal types here for the convenience of the reader. Each trivalent impurity atom may have associated with it (1) a monovalent cationic impurity atom, (2) a monovalent anion, (3) half an oxygen vacancy or (4) a positive hole, as in a semiconductor. The type of color center which forms upon irradiation depends upon the type of defect pre-existing in the solid. Hence the color may be determined more by the manner in which the impurity atom is incorporated into the lattice than by the chemical identity of the atom. Of course the manner of incorporation is partially affected by the chemical identity of the impurity atom, but it is also affected by other variables such as direction of crystal growth (12) and availability of other impurity atoms. For example variations in direction of crystal growth are probably responsible for the patterns in Fig. 1.

Confining our attention to the first two types of impurity configurations, one would expect the relative concentration of each type to be determined by conditions which exist when the material is formed in nature or prepared in the laboratory. The availability of monovalent cations such as Na^+, the availability of monovalent anions (principally OH^-), the tendency of the trivalent impurity atom (Al^{+++} or Fe^{+++}) to bind either the monovalent anion or cation, and the ease with which the trivalent impurity can be incorporated substitutionally into the lattice will be the principal factors determining the number of different types of centers formed. Studies of silica alumina cracking catalysts have shown that they lose their last traces of water only with great difficulty (13), and that the hydroxyl groups in these catalysts are associated essentially with the aluminum atom (14). One may therefore assume that the gels with an aluminum impurity prepared in this laboratory contain predominantly defects of the second type. Iron, on the other hand, has comparatively little tendency to bind water, or more correctly hydroxyl groups chemically, (15) hence one would expect iron-containing gels to possess more defects of other types. Although iron is not as easily incorporated substitutionally into a silica lattice as aluminum is, the incorporation of a few tenths of a per cent of iron as a simple substitute for silicon should pose no problem. However, the tendency for iron to form local iron silicate structures is more marked than for aluminum to form similar aluminum silicate structures.

Another noticeable trend is that, in general, highly ordered (crystalline) silicas tend to turn smoky upon irradiation, whereas disordered or highly defective structures tend to turn amethystine. The only crystalline silicas which turn purple on irradiation are decolorized natural amethysts (which, incidentally, are highly d-l twinned). All attempts to produce amethyst in the laboratory have failed so far. On the other hand, noncrystalline silicas generally turn purple when irradiated, the only exceptions being the smoky silica gel described herein, the fused material obtained from it, and a few agates. Heating to a high temperature (8, 10) which would tend to create more general disorder seems to enhance the possibility of producing amethyst coloration by irradiation in impure fused silicas.* (16) Hence, general disorder as well as specific defect-impurity structures may well be responsible for the amethyst radiation coloration.

Concerning the coloration of natural minerals, it has already been pointed out (17) that the absorption spectra and fading characteristics of natural smoky quartz are different from these properties of smoky quartz prepared in the laboratory. This agrees with our findings concerning the patterning of some samples of natural smoky quartz, and their response to ultra violet light and to gamma irradiation. Although it is possible that the effects of aging for geological periods of time might alter these characteristics somewhat, or that other means of excitation and ionization may produce superficially similar color centers, it would certainly appear that the color centers in many naturally occurring smoky quartz and amethyst specimens are not similar to those produced by ionizing radiations. Concerning amethyst, one need only note that different amethyst samples also respond differently to irradiation and to ultraviolet light, in addition to the fact that many amethysts (particularly those deposited hydrothermally in geodes and vugs) have never been associated with natural radioactivity.

SUMMARY

Color centers in both natural and synthetic silicas are associated with impurity atoms although, since impure silicas do not always form color centers upon irradiation, these impurities per se are not sufficient to cause coloration. For trivalent impurities the extent and type of coloration seems to depend more upon the manner of incorporation rather than the identity of the impurity atom, although the identity will naturally affect the type of center formed. The degree of general disorder may be

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* An interesting exception to this is reactor irradiated quartz, which at first darkens, but then becomes bleached at an exposure of $\sim 10^{10}$ n.v.t. Observable disorder does not begin until exposures of $\sim 3\times 10^{19}$ n.v.t. The effects of neutron irradiation however would be expected to differ from the effects of heating in as much as the former would disrupt individual atoms, and the latter would disorder the relationship between SiO_4 tetrahedra.

important, but specific defects, especially hydroxyl ions associated with positive hole traps, should also be considered. The difference in behavior between some natural specimens and those prepared or treated in the laboratory makes it doubtful that some of these natural quartz specimens were originally colored by ionizing radiation.

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REFERENCES

1. J. JOLY, *Phil. Mag.*, Series 6, 13 (1907); C. DOELTER, "Das Radium und die Farben," Steinkopff, Dresden, 1910.
2. A recent bibliography has been compiled by R. BECHMANN, *Nucleonics*, **16**, No. 3, 122, 1958.
3. H. W. KOHN, *Nature*, **184**, 630, 1959.
4. H. W. KOHN AND E. H. TAYLOR, International Conference on Catalysis, Paris, 1960.
5. J. A. GHORMLEY AND C. J. HOCHANADEL, *Rev. Sci. Inst.*, **22**, 473 (1951).
6. C. J. HOCHANADEL AND J. A. GHORMLEY, *J. Chem. Phys.*, **21**, 880 (1953).
7. F. H. POUGH AND T. H. ROGER, *Am. Mineral.*, **32**, 31 (1947).
8. R. YOKOTA, *J. Phys. Soc., Japan*, **7**, 222, 316 (1952).
9. A. J. COHEN, *J. Chem. Phys.*, **25**, 908 (1956); *Am. Mineral.*, **41**, 874 (1956); A. J. COHEN AND C. G. SUMMER, *Am. Mineral.*, **43**, 58 (1958).
10. A. KATS, Fourth International Congress on Glass, Paris, 1956, 400; A. KATS AND J. M. STEVELS, *Phillips Res. Repts.*, **11**, 115 (1956); J. M. STEVELS AND A. KATS, *ibid.*, **11**, 103 (1956).
11. E. F. HOLDEN, *Am. Mineral.*, **10**, 203 (1925).
12. F. AUGUSTINE AND D. R. HALE, *J. Chem. Phys.*, **29**, 685 (1959).
13. R. G. HALDEMAN AND P. H. EMMETT, *J. Am. Chem. Soc.*, **78**, 2917 (1956).
14. H. G. WEISS, J. A. KNIGHT AND J. SHAPIRO, *ibid.*, **81**, 1823 (1959).
15. P. W. SELWOOD, M. ELLIS AND C. F. DAVIS, JR., *ibid.*, **72**, 3549 (1950); P. W. SELWOOD, M. ELLIS AND K. WETHINGTON, *ibid.*, **71**, 2181 (1949).
16. R. A. WEEKS AND C. M. NELSON, private communication.
17. N. E. VEDENEEVA AND E. S. RUDNETSKAYA, *Doklady Akad. Nauk., S.S.S.R.*, **87**, 361 (1952), *C.A.* **47**, 6259 (1953); L. G. CHENTSOVA AND N. E. VEDENEEVA, *Doklady Akad. Nauk., S.S.S.R.*, **60**, 649 (1948); *C.A.* **43**, 8785 (1949).

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