American Mineralogist, Volume 71, pages 95–98, 1986

A spectroscopic study of blue radiation coloring in plagioclase

ANNE M. HOFMEISTER[1] AND GEORGE R. ROSSMAN

Division of Geological and Planetary Sciences[2]
California Institute of Technology 170-25
Pasadena, California 91125

Abstract

Blue color in sodic plagioclase is produced by electronic transitions of Pb in a manner similar to the mechanism causing color in amazonite (potassium feldspar colored blue-green by Pb electronic transitions). The two blue feldspar varieties have the following characteristics in common: (1) elevated Pb concentrations (usually greater than 0.01 wt.%), (2) structurally incorporated H^+, (3) similar response of the color to heating and irradiation, and (4) similar band shape, position, and polarization in the optical spectrum.

Introduction

Pale blue, somewhat turbid plagioclase feldspar is frequently found near the pocket zones of pegmatites. Occasionally pegmatites contain centimeter sized, nearly gem-quality masses of distinctly blue albite or oligoclase. Based on the similarity of plagioclase reflection spectra to those of blue to green potassium feldspar (amazonite), Rudenko and Vokhmentsev (1969) suggested that the pale blue color in sodic plagioclase arises from the same mechanism. This study presents absorption-spectroscopic, chemical, and physical data on blue albite and oligoclase from several different localities and compares the results to amazonite in order to elucidate the coloring mechanism in blue plagioclase.

The following summarizes the properties of blue to green potassium feldspar: Color in amazonite can be removed by heat and restored by radiation (Eliseev, 1949). All amazonites have elevated amounts of Pb, although not all Pb-bearing feldspars are blue-green (Foord and Martin, 1979; Foord, Martin, Cocklin, and Simmons, in prep.). Hofmeister and Rossman (1985a) have shown for potassium feldspar that: (1) Ionizing radiation produces smoky color if structurally bound H_2O is not present, blue-green color if both Pb and structurally bound water are present, but no color if H_2O is present and Pb is not. (2) Blue to green colors of amazonite result from electronic transitions of Pb^+ or Pb^{3+}. (3) Radiation can form the chromophore only from Pb^{2+} which has H_2O structurally bound nearby. (4) High Pb content (greater than 1000 ppm) in microcline is associated with distortion of some of the M-sites to resemble those found in orthoclase.

Methods

Quantitative chemical analyses were made using an automated MAC-5-SA3 electron microprobe. Semi-quantitative analyses for trace elements were taken with a Kevex Micro-X 7000 energy-dispersive X-ray fluorescence (XRF) spectrometer.

Polarized visible to near-infrared spectra were obtained in a Cary 17I spectrometer from optically oriented slabs of feldspar. Polarized infrared (IR) spectra were obtained from the same slabs in a Perkin Elmer 180 spectrometer. Electron paramagnetic resonance (EPR) spectra were taken on powders at liquid nitrogen temperature with a Varian E-line spectrometer at about 9.2 GHz. All spectral data were digitized and scaled. Visible spectra are corrected for instrumental baselines.

Results

Visible absorption spectra of gem-quality blue oligoclase (Fig. 1), gem-quality blue albite (Fig. 2), and clouded blue cleavelandite show that the blue color arises from a broad band similar to that which produces amazonite color in potassium feldspar (Fig. 2). All naturally blue sodic plagioclases, both gem-quality and turbid, have one band which is centered at 625 to 654 nm, has a full width at half height (FWHH) of about 4000 cm^{-1}, and an intensity that varies from 0.17 (albite, 31) to 0.27 per cm (albite, 30) in the beta direction (Table 1). The similarity of spectra in the albites, which are of a low structural state (indicated by the pegmatitic occurrence and the infrared spectra of sample 31) to that of the oligoclase, which is an *e*-plagioclase (Gay, 1955), suggests that the chromophores are in structurally similar sites that are independent of the differences in the plagioclase structures. The similarity of spectra from turbid and clear specimens shows that the color is intrinsic and not due to inclusions or secondary phases.

The absorption band is asymmetric and most intense in beta, which is nearly perpendicular to (001), weak in alpha, which is nearly perpendicular to (010), and absent in gamma. This is the same as the spectra of amazonite which also has beta nearly perpendicular to (001) and

---

[1] Present address: Geophysical Laboratory, Carnegie Institution of Washington, Washington, D.C. 20008.

[2] Contribution number 4060.

0003–004X/86/0102–0095$02.00

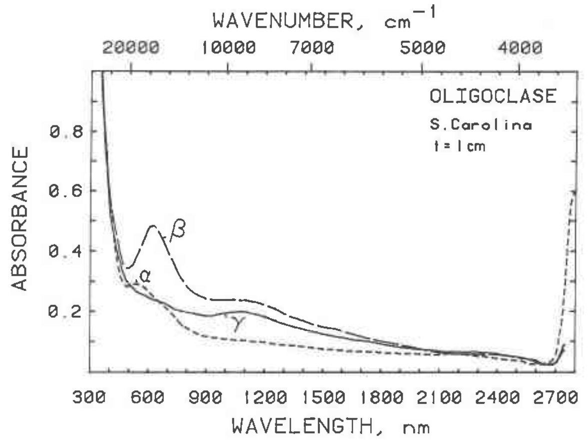

Fig. 1. Polarized absorption spectra of gem-quality pale blue oligoclase 29 that was first irradiated (1.17 MRads) and then sunbleached (5 days). These spectra are essentially identical to untreated blue plagioclase. Scaled for 1.0 cm thickness. The blue color results from the polarized band at 625 nm. The weak band at about 1100 nm is probably ferrous iron. The weak band near 2300 nm is due to OH⁻.

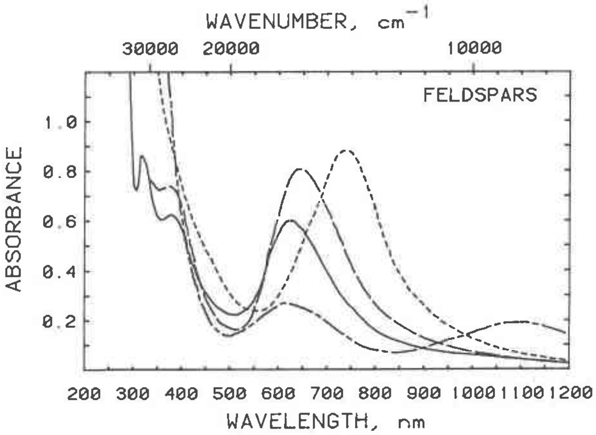

Fig. 2. Comparison of the visible spectra of the beta polarization of albite with three varieties of amazonite. Dash-dotted line, albite 30 scaled for 20 mm thickness. Solid line, blue microcline from Lake George, Colorado. Dotted line, green orthoclase from Broken Hill, Australia. Dashed line, blue-green microcline from pegmatites near Keivy, USSR. Spectra from the potassium feldspars are scaled for 0.50 mm thickness. A fourth type of spectra, consisting of the superposition of the blue microcline and the orthoclase spectra, produces blue-green color in microcline.

alpha nearly perpendicular to (010). Because the appearance of the spectra are similar with respect to the crystallographic axes, the complete polarization (requiring 6 directions: Dowty, 1978) was not established. FWHH for the plagioclases (4000 cm^{-1}) is larger, but comparable, to that of the near-IR bands in potassium feldspar (3200 to 3750 cm^{-1}). The position of the band in plagioclase is closer to that in microcline (625 nm) than to the band position in orthoclase (720 nm). However, plagioclase, like orthoclase, exhibits only one transition at wavelengths longer than 300 nm, rather that having three bands as observed in microcline. If the same mechanism operates in coloring plagioclase, then the appearance of the spectra suggests that the splitting of the chromophore's energy levels is large as in orthoclase, but that the lowest energy transition is relatively high as in microcline.

Table 1. Sample description, composition, and absorption spectral data

Feldspar	Oligoclase	Albite	Albite	Albite, Variety Cleavelandite	Albite
Locality	S. Carolina	Kenya	Mozambique	Blue Lady Mine San Diego Co., CA	Kenya
Sample No.	29 HMM 81228	30	31	33	34 NMNH 126034
Description	Gemmy Pale blue	Gemmy Pale blue	Near gemmy Light blue	Clouded Pale blue	Gemmy Pale blue
Electron Microprobe Analysis					
SiO_2	62.0	67.22	67.87	67.18	66.66
TiO_2	ND	BLD	BLD	BLD	BLD
Al_2O_3	22.76	20.69	19.13	19.49	21.12
FeO_{total}	0.04	BLD	BLD	BLD	BLD
MgO	BLD	BLD	BLD	BLD	BLD
BaO	BLD	0.11	BLD	BLD	BLD
CaO	3.82	1.40	0.03	0.09	1.39
Na_2O	10.51	11.03	12.69	12.08	11.65
K_2O	0.31	0.20	0.05	0.16	0.19
PbO	trace	ND	0.06	BLD	0.05
Total	99.65	100.68	100.08	99.08	101.09
OR	1.6	1.1	0.3	0.8	1.0
AB	82.0	92.4	99.6	98.8	92.9
AN	16.4	6.5	0.1	0.4	6.1
XRF Analysis					
Fe	0.050	0.026	ND	0.011	0.031
Pb	0.035	0.018	ND	0.002	0.009
SrO	0.04	BLD	0.18‡	0.01	0.017
Absorption Spectra Data					
Position, nm	625	630	654	642	626
Absorbance, cm^{-1}	0.22	0.27	0.17	0.3*	0.22

Analyses in weight %, except for An-Ab-Or which are in mole %. BLD, below limits of detection. ND, not determined. NMNH, National Museum of Natural History, Smithsonian Institution. HMM, Harvard Mineralogical Museum, Cambridge, MA. ‡By microprobe analysis. *This value overestimates the intrinsic absorbance per cm because of multiple reflections within the polycrystalline material.

Other features sometimes present in blue plagioclase, but not connected with the color, are (1) sharp bands at 383 and 421 nm which indicate ferric iron in tetrahedral sites, and a weak broad band at 1100 to 1200 nm which indicates ferrous iron probably in the M-site (Hofmeister and Rossman, 1984), and (2) absorption features similar to smoky color in potassium feldspar: a UV tail, which is probably due to electrons trapped at defects, and an absorption in alpha at 560 nm, which is due to one of the hole centers involving oxygen: $[SiO_4/K^+]^{2+}$, $[SiO_4/Na^+]^{2+}$ or a hole shared between two non-bonding oxygens attached to Si (Hofmeister and Rossman, 1985b), or $[AlO_4/Al^{3+}]^{3+}$ (Speit and Lehmann, 1982).

A trace of lead was indicated in the XRF analysis of all blue plagioclases, and was occasionally found in the electron microprobe analyses (Table 1). By comparing intensities of Pb lines of plagioclase to Pb lines in potassium feldspar through XRF, the lead contents were estimated within ±30% of the amount present. The amounts (~20 to 350 ppm Pb) are much higher than the usual 10 ppm Pb in plagioclase (Wedepohl, 1956) but much less than the total lead content of amazonite (170 to 18000 ppm

Pb: Foord et al., in prep.). The data in Table 1 show that like amazonite, intensity of plagioclase color is independent of Pb content. The minimum extinction coefficient must thus be calculated from the sample with the least amount of lead and the most intense color, and is estimated as 1000 liter/mole-cm. This is comparable to extinction coefficients of Pb in orthoclase (2500) and microcline (4300) and suggests that lower lead concentrations cause the much lower intensity of color in sodic plagioclase (absorbance less than 0.27 per cm) as compared to that of potassium feldspars (up to 13 per cm).

EPR spectroscopy was used to search for the Pb center in oligoclase 29, but no signature attributable to this ion was observed. Instead, the patterns seen indicate the presence of two of the hole centers associated with smoky color: $[SiO_4/Na^+]^{2+}$ and a hole shared between two nonbonding oxygens on Si (Hofmeister and Rossman, 1985b). The absence of the Pb signal does not rule out an amazonite mechanism: none was observed in orthoclase-amazonite, as a result of a range in geometries of M-sites for the chromophore which is caused by both Al/Si disorder and incorporation of high amounts of Pb (Hofmeister and Rossman, 1985a). Because the blue oligoclase has an intermediate structural state (i.e., it is an *e*-plagioclase: Gay, 1955) it would also offer many different M-sites that Pb could occupy. Thus, the structure of the oligoclase probably prevented direct confirmation of Pb as the chromophore. The similarity of the albite optical spectrum to that of the oligoclase suggests that albite also has multiple sites for the chromophore which would prevent EPR detection. For potassium feldspars, incorporation of about 1000 ppm Pb results in distortion of the M-site (Hofmeister and Rossman, 1985a). It is likely that smaller amounts of Pb would have a similar effect on plagioclase because it accepts lead less readily than $KAlSi_3O_8$ (Smith, 1974, p. 103) and because its smaller M-site would need to distort more to accommodate the Pb ion.

Structurally bound water molecules were not detected in gem-quality plagioclase by IR spectroscopy. Instead, the IR spectra (Fig. 3) show broad bands at 3600, 3450, and 3170 cm^{-1} that are similar to OH^- bands in sanidine (Hofmeister and Rossman, 1985b). This assignment is corroborated by the absence of H_2O stretch-bend combination modes near 5260 cm^{-1} (1900 nm; Fig. 1), and by the existence of variable amounts of OH^- in all plagioclases investigated so far by infrared spectroscopy (Solomon and Rossman, 1982). Comparison of band intensities of oligoclase to those of sanidine with OH content measured by hydrogen manometry (Hofmeister and Rossman, 1985b) allowed estimation of the oligoclase's OH concentration as 0.02 wt.% H_2O. Comparison of the oligoclase spectra to that of molecular water in microcline suggests that molecular H_2O in oligoclase is less than 0.00002 wt.%. Concentrations of structural water in amazonite are considerably larger (0.0002 to 0.0035 wt.% H_2O: Hofmeister and Rossman, 1985a). Because intensity of color in plagioclase is 50 times smaller than that of potassium feldspar, it is conceivable that very small amounts of molecular water are involved in plagioclase coloration, such that the small amounts of H_2O not of Pb result in the weak coloration of plagioclase. However, irradiation behavior of blue plagioclase suggests otherwise. When irradiated, blue plagioclase develops a smoky color and a spectrum similar to that of irradiated anhydrous $KAlSi_3O_8$. This color forms in $KAlSi_3O_8$ only if molecular water is absent (i.e., less than our detection limits).

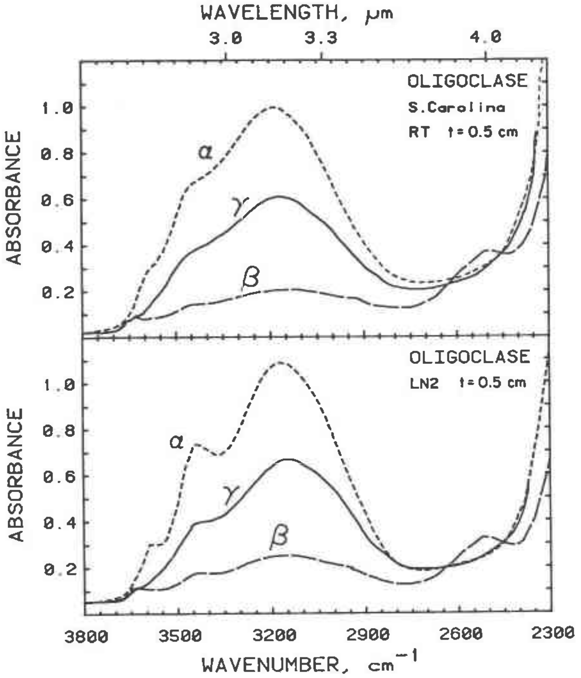

Fig. 3. Polarized IR spectra of gemmy, pale blue oligoclase 29 taken at room and liquid nitrogen temperatures. Absorptions at 3700, 3450, and 3180 cm^{-1} are due to different types of OH^-. The small change upon cooling shows that only a small proportion of the hydrogen ions can be present as fluid inclusions. Lattice overtones occur near 2500 cm^{-1}.

Rudenko and Vokhmentsev (1969) demonstrated that the blue color of two Russian oligoclases was totally removed by heating one to 300° and the other to 600° for 24 hours, but was not returned by X-ray irradiation. Total destruction of color by heating at some temperature is expected for an amazonite mechanism because hydrous impurities are an essential ingredient for color and sufficient heating will dehydrate the sample: once dehydrated, Pb-bearing potassium feldspar never regains its original blue color regardless of radiation dose (Hofmeister and Rossman, 1985a). With careful heating steps, the color of the blue plagioclase can be partially removed. Sample 30 lost about one half of the intensity of the 630 nm band after being heated at 300°C for 25 minutes (Fig. 4), and all its color after 12 hours at 500°C.

The involvement of radiation in plagioclase coloring is demonstrated by the restoration of blue color in partially heat-bleached albite 30 by exposure to ionizing radiation (Fig. 4c). The crystals are initially orange after 26.6 MRads

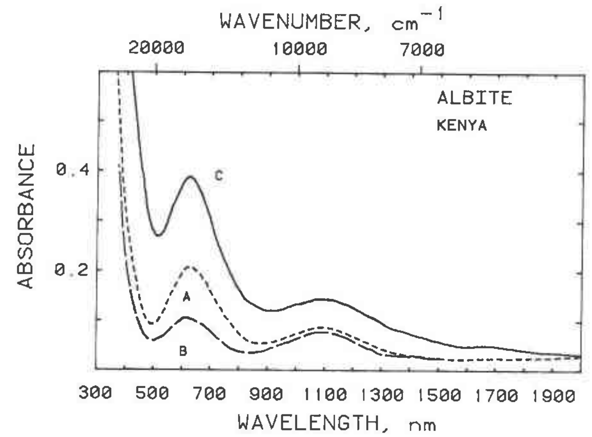

Fig. 4. Absorption spectra in the beta direction of albite 30, scaled for 7.0 mm thickness. (A) Original crystal. (B) Color partially removed by heating at 300°C for 25 minutes. (C) Color restored by irradiating with 26.6 Mrads ^{137}Cs gamma rays followed by exposure to intermittant sunlight for one week. Fe^{2+} absorption occurs near 1100 nm.

of ^{137}Cs gamma rays, due to the tail of an intense absorption in the UV (Fig. 4b). This absorption is similar to the smoky coloration in sanidine which results from electrons trapped probably at O^{2-} vacancies, and from the hole centers $[AlO_4/Al^{3+}]^{3+}$ (Speit and Lehmann, 1982), $[SiO_4/K^+]^{2+}$, and a hole shared between two non-bonding oxygens attached to Si (Hofmeister and Rossman, 1985b). Exposure to sunlight removes the UV absorption but does not affect the 630 nm band. The spectrum in Figure 4c was obtained from a crystal partially bleached by exposure to intermittent sunlight for one week; some of the UV component remains and contributes to the overall level of absorption.

Irradiation and OH^- by themselves do not cause blue color. Andesine from Halloran Springs, California, that has 0.05 wt.% OH, but no lead detectable by XRF (less than about 20 ppm Pb) produces only the smoky color upon irradiation. The involvement of a hydrous species in blue plagioclase coloration is suggested by the response to thermal treatment. Blue albite 30 becomes colorless when heated to 500°C, but subsequent irradiation (23 Mrad) produces an orange-brown color that reverts to the original blue upon exposure to sunlight for 12 days. When this sample was decolorized by heating at 800°C for 60 hours, subsequent irradiation turned the crystal orange-brown. However, even though exposure to sunlight faded the brown color, the blue color was not restored. This behavior is analogous to the failure of amazonite to recolor after irreversible dehydration. However, infrared spectra did not indicate that dehydration had occurred in the nearly 7 mm thick plagioclase crystal, although changes in the relative intensities of the various components of the IR spectra were seen. This behavior, while not as definitive as the case for H_2O participation in amazonite coloration, still suggests that both OH^- and Pb are essential for blue color to form in plagioclase.

Conclusions

Based on similarites of band shape, position, width and polarization, the response to irradiation and heating, and on the presence of lead in blue sodic plagioclase, we conclude that Pb coloration occurs in these minerals as in blue-green potassium feldspars. The paler color in plagioclase is most likely due to lower Pb concentrations.

Acknowledgments

This work was supported in part by NSF grant EAR-79-19987. We thank C. Bridges (Nairobi), C. Francis (Harvard), W. Larson (Pala International), and J. White (Smithsonian Institution) for providing samples; C. Martin, D. Blair, and S. Chan (Caltech) for advice with EPR spectroscopy; and Eric Dowty (American Museum of Natural History), Kurt Nassau (Bell Laboratories), and Martha Schaefer (Geophysical Laboratory) for helpful comments on the manuscript.

References

Dowty, E. (1978) Absorption optics of low-symmetry crystals-application to titanian clinopyroxene spectra. Physics and Chemistry of Minerals, 3, 173–181.

Eliseev, E. N. (1949) Obraska amazonita. Zapiski Vsesoyuzuogo Mineralogisheskogo Obshchestva, 78, 26–39 (not seen, extracted from Mineralogical Abstracts, 11, 285).

Foord, E. E., and Martin, R. F. (1979) Amazonite from the Pikes peak batholith. Mineralogical Record, 10, 373–382.

Gay, P. (1955) The structures of the plagioclase feldspars: VI. Natural intermediate plagioclases. Mineral Magazine, 31, 21–40.

Hofmeister, A. M. and Rossman, G. R. (1984) Determination of Fe^{3+} and Fe^{2+} concentrations in feldspar by optical absorption and EPR spectroscopy. Physics and Chemistry of Minerals, 11, 213–224.

Hofmeister, A. M. and Rossman, G. R. (1985a) A spectroscopic study of amazonite: irradiative coloring of structurally hydrous, Pb-bearing feldspar. American Mineralogist, 70, 794–804.

Hofmeister, A. M. and Rossman, G. R. (1985b) A model for the irradiative coloring of smoky feldspar and the inhibiting influence of water. Physics and Chemistry of Minerals, 12, 324–332.

Rudenko, S. A. and Vokhmentsev, A. Ya. (1969) Plagioclase-amazonite. Doklady Akademii Nauk SSSR, 184, 422–424 (transl. Doklady Akademii Nauk Translations, 184, 113–115).

Solomon, G. C. and Rossman, G. R. (1982) Water in feldspars. Geological Society of America Abstracts with Programs, 14, 622.

Smith, J. V. (1974) Feldspar Minerals: II. Chemical and Textural Properties. Springer-Verlag, Heidelberg.

Speit, B. and Lehmann, G. (1982) Radiation defects in feldspars. Physics and Chemistry of Minerals, 8, 77–82.

Wedepohl, K. H. (1956) Untersuchungen zur Geochimie des Bleis. Geochimica et Cosmochimica Acta, 10, 69–148.

Manuscript received, May 29, 1984;
accepted for publication, September 9, 1985.