

Vanadium- and chromium-bearing andalusite: Occurrence and optical-absorption spectroscopy

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ABSTRACT

A graphitic quartz-muscovite schist in the Llano uplift of central Texas bears euhedral porphyroblasts of andalusite with unusual yellow-to-colorless pleochroism. They contain, by weight, up to 0.81% V_2O_3 and 0.12% Cr_2O_3 , but less than 0.07% Fe_2O_3 , 0.22% TiO_2 , and 0.004% Mn_2O_3 . Optical absorption spectra in all principal vibration directions are dominated by an intense charge-transfer band in the ultraviolet, on which are superimposed broad absorption maxima at 420 and 565 nm (intense in α but weaker in β and γ), and broad maxima at 745 and 370 nm (without strong polarization dependence). The intensity of each of these absorption bands is quantitatively correlated with V + Cr content. Weak absorption is also observed in the γ spectrum near 320 nm. Assignment of the bands at 320, 420, and 565 nm to V^{3+} and Cr^{3+} in the octahedral site gives good agreement with data from other vanadian minerals for the relation of the absorption peak position to the mean bond length for the sites. The absorption peak at 745 nm probably results from octahedral V^{4+} , but the origin of the 370-nm band is uncertain. The distinctive pleochroism results from the strong polarization dependence of the 420-nm absorption band.

OCCURRENCE AND PETROGRAPHY

The unusual andalusite described here occurs abundantly as porphyroblasts in a very fine grained graphite-rich quartz-muscovite schist within the Proterozoic Honey Formation, west of Sandy Mountain in the Llano uplift of central Texas (Dunman Mountain quadrangle: Universal Transverse Mercator coordinates 14RNJ550828). The porphyroblasts are prismatic with approximately square cross sections, typically 2–3 mm wide and 5–10 mm long, but rarely as large as 10 mm wide and 80 mm in length. Although a few widely spaced fractures transect most porphyroblasts, the crystals are not fragmented. Replacement of andalusite by muscovite at crystal edges is advanced in some samples, but only incipient in others. The crystals record two separate growth episodes. Cores are inclusion-free, surrounded by a thin zone of tiny flakes of graphite and minor quartz. Rims overgrow and include mica flakes that preserve a faintly crenulated foliation, continuous with that in the matrix surrounding the porphyroblast; they also contain numerous inclusions of graphite and quartz, with the former concentrated in a cruciform pattern in some crystals. Cores are more intensely pleochroic than rims, but both display similar hues. In a section 0.03 mm thick, X = golden yellow and $Y = Z$ = colorless; in a section 0.80 mm thick, X = reddish brown and $Y = Z$ = pale yellow. The yellow pleochroic colors are distinct from the greenish-yellow hues characteristic of manganian andalusite (viridine).

CHEMICAL COMPOSITION

Electron-microprobe analysis revealed highly unusual concentrations of minor elements: V and Cr are abnormally abundant, whereas Mn, Fe, Ti, and Mg are present at lower levels than are typical of strongly pleochroic andalusites. Figure 1 shows the concentration of these elements in a traverse from core to rim across a carefully centered section through a strongly colored porphyroblast. These concentrations were determined on a JEOL 733 instrument using wavelength-dispersive techniques. Standards were a natural kyanite crystal for Al and Si, and synthetic calcium-aluminum silicate glasses (Corning Glasses V and W) that contained (in weight percent oxide) 8.69% MgO, 0.65% V_2O_3 , 0.78% Cr_2O_3 , 0.73% FeO, 0.79% TiO_2 , and 0.65% MnO. A high sample current (30 nA on brass) and long counting times (200 s for both peaks and backgrounds) were used for minor elements, in order to improve X-ray counting statistics. Enhancement of the $VK\alpha$ signal by interference from $TiK\beta$ was minimal; analyses of titaniferous V-free standards indicated that very small corrections to the V count rate (never more than minus 2% relative) were needed. Limits of detection at the 99% confidence level, in weight percent, defined according to the formulation of Le Maitre (1982), are 0.003% for V_2O_3 , 0.004% for Cr_2O_3 , 0.004% for Fe_2O_3 , 0.008% for TiO_2 , 0.004% for MgO, and 0.004% for Mn_2O_3 . Of these elements, all except Mn are present at levels well above the limit of detection.

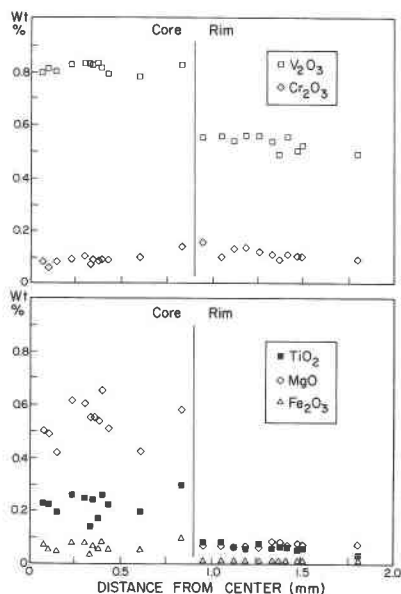


Fig. 1. Concentration profiles for trace elements in centered sections through andalusite porphyroblast.

The amounts of V and Cr in the andalusite from the Llano uplift are strikingly higher than those reported in other occurrences. Relatively few analyses in the literature include these elements, but for V_2O_5 and Cr_2O_3 , respectively, *maximum* weight percents reported are 0.01 and 0.01 by Pearson and Shaw (1960, Table 3); 0.001 and 0.001 by Albee and Chodos (1969, p. 313); 0.03 and 0.01 by Chinner et al. (1969, Table 1); 0.04 and 0.03 by Okrusch and Evans (1970, Table 2); 0.04 and 0.12 by Dodge (1971, Table 1); and 0.10 (as V_2O_5) and 0.03 by Kerrick and Speer (1988, Table 1). Thus V contents are far higher in the Llano andalusite than in any previously recorded occurrence; with the single exception of sample E-99 of Dodge (1971), Cr contents are likewise unexceeded.

The abundance of V and Cr probably results in part from a favorable bulk composition, but the concomitant low levels of Fe and Mn signify the importance of strongly reducing conditions during mineral growth. The presence of graphite at the inferred metamorphic conditions of approximately 600 °C and 2 kbar (cf. McGehee, 1979; Bebout and Carlson, 1986) requires an oxygen fugacity below $\sim 10^{-20}$ bar (French and Eugster, 1965). Oxygen fugacity was evidently sufficiently low to prevent incorporation of large amounts of ferric or manganic components, while maintaining V and Cr in the trivalent state.

OPTICAL-ABSORPTION SPECTROSCOPY

Because of their unusual chemical composition, these andalusites offer an opportunity to study the absorption spectra of V in andalusite with minimal interference from other chromophores. Polarized optical-absorption spectra were measured using techniques detailed in Rossman (1975), first on a pair of oriented specimens with a thick-

TABLE 1. Trace-element concentrations in regions used for optical spectroscopy

Oxide	Core (wt%)	Rim (wt%)
V_2O_5	0.81	0.54
Cr_2O_3	0.09	0.12
Fe_2O_3	0.07	0.01
Mn_2O_3	n.d.	n.d.
TiO_2	0.22	0.06
MgO	0.52	0.07

Note: n.d. = below detection limit of 0.004 wt%.

ness of ~ 0.53 mm and then on the same specimens after thinning them to ~ 0.11 mm. For each specimen, spectra were measured in the α , β , and γ directions through a circular area ~ 0.5 mm in diameter in a region near the crystal's core and in another region near its rim. The averages of ten microprobe analyses for trace elements in the center of each region are presented in Table 1.

The spectra on which absorption measurements were made are replicated in Figures 2a–2c, and those measurements are summarized in Table 2. Each spectrum is dominated by an intense band in the ultraviolet (presumably metal-oxygen charge-transfer) that extends into the visible region. Superimposed on this feature are several weaker absorption maxima. The unusual pleochroism of these crystals is the result of intense absorption in the α direction centered at 420 nm (Fig. 2c); the absorption at this wavelength has much lower intensity in the β and γ directions (Fig. 2a). Weaker absorption is also recorded near 745, 565, and 370 nm; near 320 nm, a very weak absorption maximum is noted only in the γ spectrum of the thinner section (not illustrated).

Interpretation of these spectra is facilitated by the fact that V is far more abundant than any other trace element. In addition, because the absorption maxima for octahedral Cr^{3+} are expected to nearly coincide with those of octahedral V^{3+} [as they do, for example, in corundum (cf. McClure, 1962), and many other minerals (cf. Schmetzer, 1982)], the effects of the two elements are essentially ad-

TABLE 2. Summary of optical spectroscopy

Polarization direction	Peak position (nm)	Sample thickness (mm)	Abs [core]	Abs [rim]	Abs[core] to Abs[rim] ratio	ϵ [core] ($L \cdot mol^{-1} \cdot cm^{-1}$)	ϵ [rim]
α	n.o.						
β	n.r.						
γ	370	0.534	0.17	0.12	1.4	17	16
α	420	0.106	0.70	0.54	1.3	350	360
β	n.r.						
γ	420	0.534	0.13	0.10	1.3	13	13
α	565	0.106	0.13	0.10	1.3	64	67
β	565	0.534	0.14	0.09	1.6	14	12
γ	565	0.534	0.05	0.03	1.7	5	4
α	n.r.						
β	750	0.534	0.09	0.06	1.3	9	8
γ	740	0.534	0.04	0.03	1.3	4	4

Note: Abs = absorbance above background; n.o. = not observable above background; n.r. = observable above background, but not resolved sufficiently for measurement.

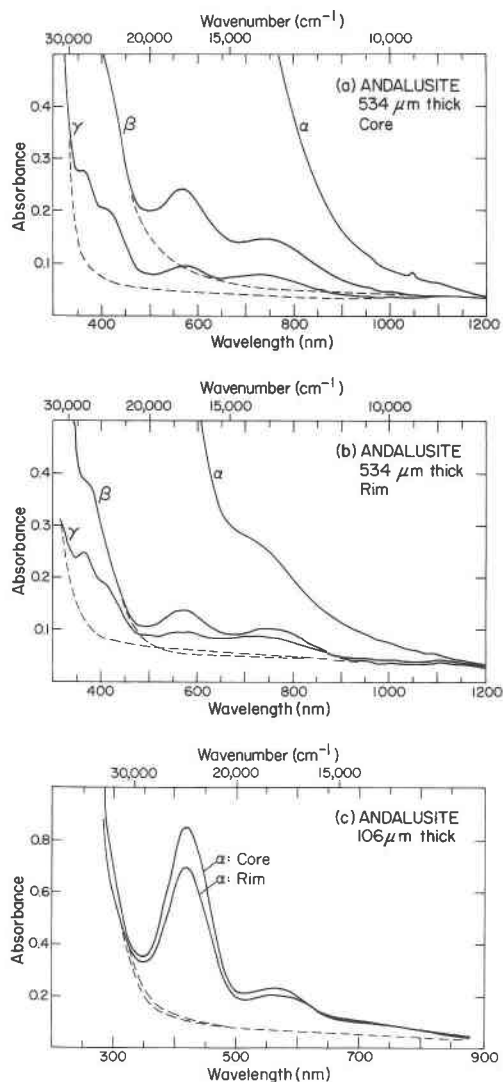


Fig. 2. Polarized absorption spectra of Llano andalusite. Dashed lines are estimates of background, above which absorption-peak intensities were measured. Note differences in scales for part (c).

ditive when superimposed in these spectra. The data of Table 1 (converted to molar proportions) and of Table 2 confirm that the four most prominent absorption maxima in these spectra are the result of the combined effects of V and Cr, insofar as increases in absorption from rim to core correlate quantitatively with increases in the molar concentration of V summed with Cr. Both molar concentration and absorption intensity are greater in the core than in the rim by a factor of about 1.3 to 1.4. Two larger values for this absorption intensity ratio appear in Table 2; these arise from measurements on very low intensity peaks, for which small errors in the estimated background are magnified into larger uncertainties in the intensity ratios. [It is unlikely that either Fe^{3+} or the Fe^{2+} - Ti^{4+} intervalence charge transfer contributes importantly to the

spectra. The more probable interference, Fe^{2+} - Ti^{4+} intervalence charge transfer, is centered near 480 nm (Faye and Harris, 1969; Smith, 1977), which is a region of particularly low absorbance in the spectra of the Llano andalusite.]

Most solids in which V^{3+} replaces Al^{3+} in octahedral coordination are characterized by optical-absorption spectra dominated by two broad maxima: one in the range 540–660 nm, the other in the range 370–450 nm (Schmetzer, 1982). The systematic relation between the positions of these two absorption peaks and the mean bond lengths in trivalent cation sites, as shown in Figure 5 of Schmetzer (1982), indicates that the peaks at 420 and 565 nm in the andalusite spectrum arise from V^{3+} in the octahedral site. The 320-nm peak in the andalusite spectrum corresponds to a peak near 300 nm in the spectrum of vanadial corundum (McClure, 1962), implying that this short-wavelength absorption maximum in andalusite also originates from octahedral V^{3+} . The bands at 565, 420, and 320 nm correspond respectively to transitions from the ${}^3T_{1g}$ state to the ${}^3T_{2g}$, ${}^3T_{1g}$, and ${}^3A_{2g}$ excited states of V^{3+} .

The 745-nm absorption peak in the andalusite spectrum correlates closely with peaks observed in the spectra of vanadial zoisite and roscoelite; Schmetzer (1982, p. 90 and 94) has argued that these bands are analogous to those present in the spectra of solids with octahedral V^{4+} and aqueous solutions containing the oxovanadium complex VO^{2+} (Jorgensen, 1957; Grum-Grzhimailo and Shcherbina, 1961). A weaker band near 590 nm arising from octahedral V^{4+} (Jorgensen, 1957; Ballhausen and Gray, 1962) could account for the asymmetry to the long-wavelength side of the band at 550–600 nm in the spectra of Llano andalusite.

Assignment of the 370-nm band remains problematic. Although we note that Fe^{3+} frequently absorbs in the 375-nm region, the absorption intensity in Llano andalusite at this wavelength is proportional to the molar concentration of V summed with Cr and does not correlate with Fe content. We also note that absorption maxima near 350 nm are reported by Grum-Grzhimailo and Shcherbina (1961) for the V^{5+} compounds NaVO_3 and KVO_3 , and for aqueous solutions containing V^{5+} complexes. Likewise, Platonov et al. (1971) observed intense absorption between 345 and 370 nm in the spectra of three minerals characterized by tetrahedral V^{5+} (vanadinite, descloisite, and brackebuschite). Although the presence of V^{5+} in this graphitic occurrence is regarded as somewhat unlikely, absorption by V^{5+} in tetrahedral sites is a possible, but speculative, origin for the 370-nm band in the spectra of the Llano andalusite.

CONCLUSIONS

The combination of a bulk composition enriched in V and Cr with low oxygen fugacity during crystal growth has produced andalusite crystals of unique chemical composition and pleochroism. The incorporation of V^{3+} and Cr^{3+} in octahedral sites leads to absorption maxima at

320, 420, and 565 nm. Octahedral V^{4+} is the most likely source of the absorption near 745 nm, but an origin for the 370-nm band cannot be identified definitively. The unusual yellow-to-colorless pleochroism is attributed to the strong polarization dependence of the absorption for wavelengths near 420 nm.

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