

*Origin of optical pleochroism in orthopyroxenes*

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*Summary.* The necessary conditions for optical pleochroism in orthopyroxenes are: ordering of  $\text{Fe}^{2+}$  ions, with preferential occupation of  $M_2$  positions; presence of small, high-valence cations ( $\text{Al}^{3+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Ti}^{4+}$ ) in  $M_1$  positions; replacement of Si by Al; and a sufficient  $\text{Fe}^{2+}$  content. These factors favour an intensification of the charge-transfer absorption bands in the ultra-violet that is more marked for the  $\alpha$  vibration direction than for  $\beta$  and  $\gamma$ . This leads to absorption in the blue and a red colour in transmitted  $\alpha$ -polarized light, while  $\beta$  and  $\gamma$  remain green.

**T**WO distinctive features of minerals are the properties of colour and pleochroism of crystals in thin section. In many cases, the origins of colour and, in particular, pleochroism in silicates have not been explained. Measurements of polarized absorption spectra of minerals can, however, yield information on the origins of colour and pleochroism (Burns, 1965).

Most ferromagnesian silicates (olivines, orthopyroxenes, clinopyroxenes, cummingtonites, actinolites, pigeonites) are distinctly pleochroic in the short-wave infra-red region (7000–14 000 Å), but the effects are not apparent optically (Burns, 1965). The green colours generally observed in ferromagnesian silicates containing  $\text{Fe}^{2+}$  in six-fold coordination result from absorption of light in the red region by shoulders of absorption bands with maxima in the infra-red (Burns, 1965); absorption of this radiation induces  $d$  electron transitions within the  $\text{Fe}^{2+}$  ion. Pleochroism in each ferromagnesian silicate series is related to the presence of  $\text{Fe}^{2+}$  ions in distorted coordination sites, and to strong next-nearest neighbour interactions between cations along specific crystallographic directions (Burns, 1965).

Many orthopyroxenes, particularly those occurring in granulite facies and plutonic rocks, possess the diagnostic pleochroic scheme:  $\alpha$  pink or red;  $\beta$  pale yellow;  $\gamma$  green. Since  $\text{Fe}^{2+}$  ions are located in positions of six-fold coordination in the orthopyroxene structure (Warren and Modell, 1930; Byström, 1943; Ghose, 1965), the green colour associated with  $\gamma$ -polarized light is not unusual. However, the red colours observed

in most orthopyroxenes ('hypersthene')<sup>1</sup> in  $\alpha$ -polarized light appear to be anomalous.

Polarized absorption spectra of two orthopyroxenes, one a hypersthene ( $Fs_{26.1}$ ) possessing strong optical pleochroism and a high (4.35 wt. %)  $Al_2O_3$  content (Howie, 1963), the other a bronzite ( $Fs_{18.1}$ ) showing no visible pleochroism with a low (0.1 wt. %)  $Al_2O_3$  content (Burns, 1965), are illustrated in fig. 1. The spectra are similar in the short-wave infra-red region, with a notably high-intensity absorption band in the  $\alpha$ -polarized spectra. However, the shoulders of intense charge-transfer bands in the ultra-violet region are more prominent in the optically pleochroic orthopyroxene, the absorption edge associated with  $\alpha$ -polarized light spanning more of the visible region than those associated with  $\beta$ - and  $\gamma$ -polarized light. Therefore, the red colours in orthopyroxenes in  $\alpha$ -polarized light arise from absorption of blue and green radiation, resulting in transmission of red radiation.

In order to account for the optical red-green pleochroism in orthopyroxenes, it is necessary to explain the greater facility for charge transfer (inter-element electron transitions or photochemical oxidation-reduction) in  $\alpha$ -polarized light. The orthopyroxene crystal structure has two positions with six-fold coordination. The  $M_2$  positions are occupied preferentially by  $Fe^{2+}$  ions (Ghose, 1962, 1965; Ingham, 1957), and other ions, such as  $Mg^{2+}$ ,  $Al^{3+}$ ,  $Fe^{3+}$ ,  $Ti^{3+}$ ,  $Ti^{4+}$ , etc., fill the  $M_1$  positions. A (100) projection of the structure (fig. 2) shows the chains of  $(SiO_3)$  groups and a band of cations at  $x = 0.125$  that extend along the  $c$ -axis. Each  $M_2$  position has three neighbouring  $M_1$  positions, one of which lies along the  $b$ -axis. An entourage of four silicon atoms is located on the other side of the  $M_2$  position along the  $b$  axis. One lobe of each of the three  $t_{2g}$  orbitals (Orgel, 1960) belonging to  $Fe^{2+}$  in an  $M_2$  position lies in the (100) plane and projects towards an  $M_1$  position. One of these  $t_{2g}$  orbital lobes also projects towards the entourage of silicon atoms along the  $b$ -axis. The positive charge on the silicon atoms,

<sup>1</sup> Recently there has been a tendency to refer to any optically pleochroic orthopyroxene as 'hypersthene'. G. T. Prior (Min. Mag., 1920, vol. 19, pp. 51-63) drew the bronzite-hypersthene boundary at 20 mole %  $FeSiO_3$ , and is still followed by meteoriticists, to whom this boundary is particularly important (see, for example, B. Mason, 'Meteorites', New York (Wiley), 1962). A. Poldervaart (Min. Mag., 1947, vol. 28, pp. 164-72) defined hypersthene as  $(Mg,Fe)SiO_3$  with 30 to 50 mole %  $FeSiO_3$ , and has been widely followed by petrologists (see, for example, W. A. Deer, R. A. Howie, and J. Zussman, 'Rock-Forming Minerals', vol. 2, London, (Longmans), 1963). Since red-green pleochroism may be observed throughout the bronzite-orthoferrosilite composition range, there is no good precedent for a definition of hypersthene in terms of pleochroism.

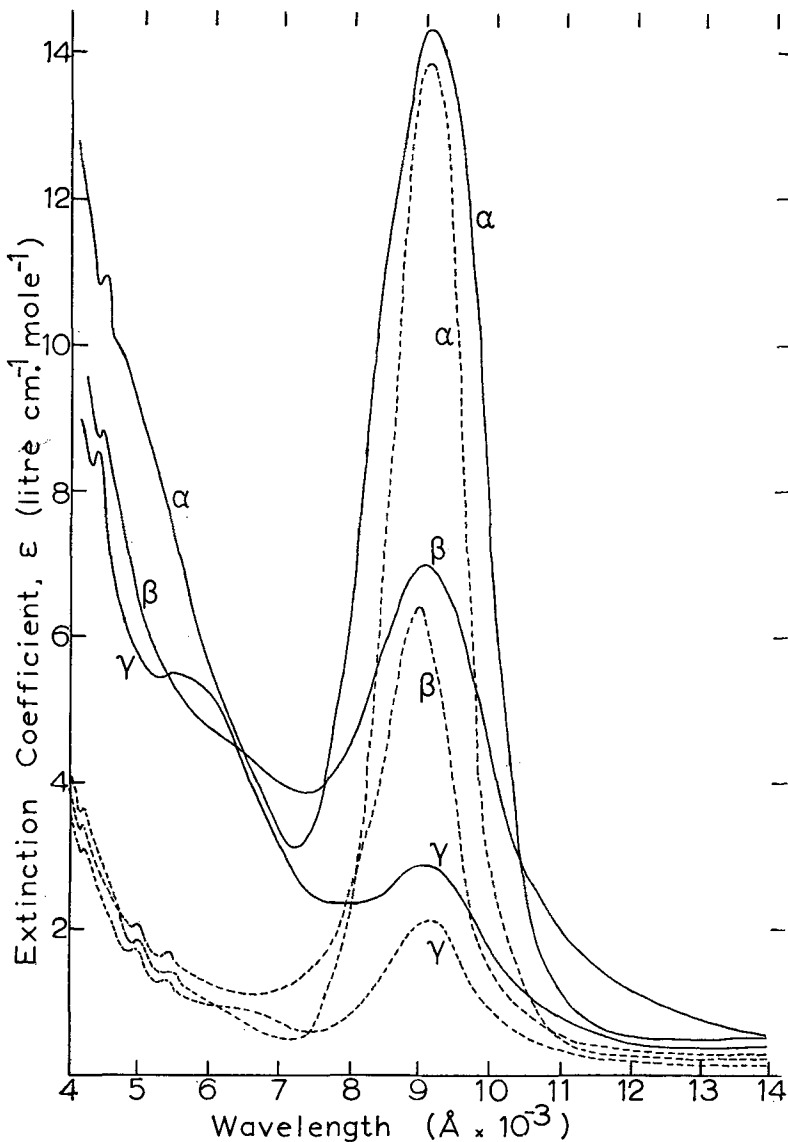


FIG. 1. Polarized absorption spectra of two orthopyroxenes, one of which displays distinct visible pleochroism (spectra in full lines), the other showing no visible pleochroism (spectra in dashed lines). Spectral measurements made with a Cary model 14 spectrophotometer using polarizing microscopes and universal stage attachments (Burns, 1966).

ideally  $\text{Si}^{4+}$ , increases the probability for  $d$  electrons to be concentrated in the  $t_{2g}$  orbital projecting along the  $b$ -axis. The presence of an  $\text{Al}^{3+}$  ion or another high valence cation ( $\text{Fe}^{3+}$ ,  $\text{Ti}^{3+}$ ,  $\text{Ti}^{4+}$ , etc.) in the  $M_1$  position adjacent to  $\text{Fe}^{2+}$  along the  $b$  axis also increases this probability.

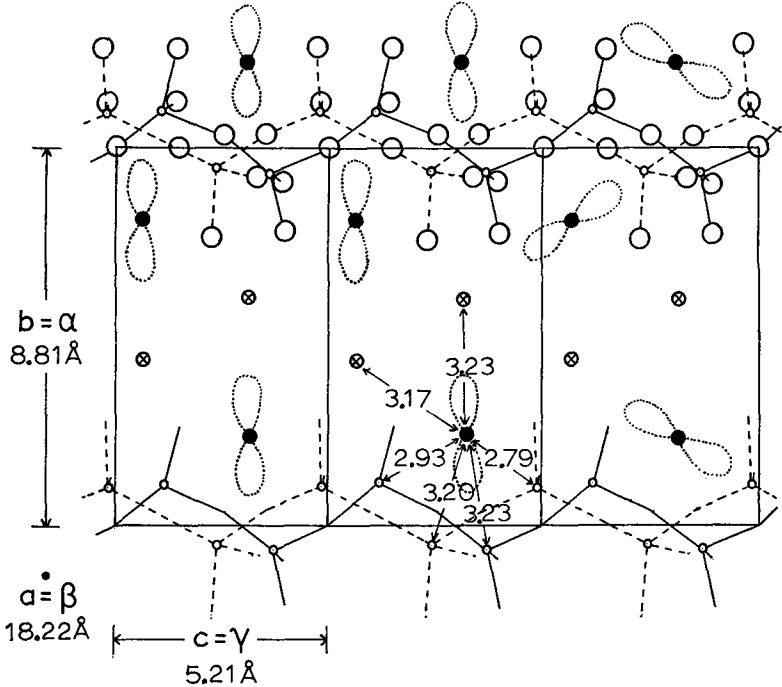


FIG. 2. Portion of the orthopyroxene crystal structure projected on to (100). Atomic coordinates and cell parameters from Byström (1943). ● cation in  $M_2$  position; ⊗ cation in  $M_1$  position; ○ silicon; ○ oxygen. Traces of lobes of  $t_{2g}$  orbitals lying in the (100) plane and belonging to  $\text{Fe}^{2+}$  ions in  $M_2$  positions are also shown.

As a result, interaction of radiation with electrons is greatest along the  $b$ -axis, and this accounts for the high absorption around  $9000 \text{ \AA}$  in the  $\alpha$ -polarized spectrum (fig. 1).

High energy ultra-violet radiation induces electron transitions between  $\text{Fe}^{2+}$  ions and silicon atoms, and between  $\text{Fe}^{2+}$  ions and cations in  $M_1$  positions. The energy needed to induce charge transfer is decreased by unbalanced electrostatic charge in a crystal structure. Charge transfer is facilitated in orthopyroxene in  $\alpha$ -polarized radiation by the presence of  $\text{Al}^{3+}$  (or  $\text{Fe}^{3+}$ ,  $\text{Ti}^{3+}$ ,  $\text{Ti}^{4+}$ , etc.) in the  $M_1$  positions

adjacent to  $\text{Fe}^{2+}$  along the  $b$ -axis. Furthermore, substitution of silicon by aluminium in  $[\text{SiO}_4]$  tetrahedra enables charge transfer to occur between  $[\text{AlO}_4]$  groups and  $\text{Al}^{3+}$  ions in  $M_1$  positions through the favourably orientated  $t_{2g}$  orbital of a  $\text{Fe}^{2+}$  ion in a bridging  $M_2$  position, the process being facilitated in  $\alpha$ -polarized light.

Therefore, necessary conditions for optical pleochroism in orthopyroxenes are:

Ordering of  $\text{Fe}^{2+}$  ions in the crystal structure, with preferential occupancy of  $M_2$  positions; this process is facilitated by crystal growth at the relatively lower temperatures of the granulite facies rather than the higher temperatures of basaltic magma.

Entry of small, high-valence cations ( $\text{Al}^{3+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Ti}^{3+}$ ,  $\text{Ti}^{4+}$ ) into  $M_1$  positions; this is favoured by high pressures (granulite facies).

Substitution of smaller silicon atoms by larger aluminium atoms in  $[\text{SiO}_4]$  tetrahedra, which is facilitated by crystal growth at high temperatures.

The  $\text{Fe}^{2+}$  ion concentration must exceed a minimum value (about 15 mole % ferrosilite).

Crystal growth under granulite-facies temperatures and pressures is most conducive to the formation of optically pleochroic orthopyroxenes.

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#### References

- BURNS (R. G.), 1965. Ph.D. Diss., Univ. of California, Berkeley.  
— 1966. Journ. Sci. Instr., vol. 43, pp. 58–60.  
BYSTRÖM (A.), 1943. Ber. deut. keram. Gesell., vol. 24, pp. 2–15.  
GHOSE (S.), 1962. Amer. Min., vol. 47, pp. 388–94.  
— 1965. Zeits. Krist., vol. 122, pp. 81–99.  
HOWIE (R. A.), 1963. Min. Soc. Amer., Spec. Pap. no. 1, pp. 213–22.  
INGHAM (K.), 1957. M.Sc. Thesis, Univ. of Manchester.  
ORGEL (L. E.), 1960. An Introduction to Transition-Metal Chemistry: Ligand-Field Theory. Methuen and Co., Ltd., London. 180 pp.  
WARREN (B. E.) and MODELLE (D. I.), 1930. Zeits. Krist., vol. 75, pp. 1–14.

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