

Crystal Structure Refinement and Optical Properties of a Ti^{3+} Fassaite from the Allende Meteorite¹

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Abstract

A pyroxene from the Allende meteorite has $C2/c$ symmetry, $a = 9.80 \pm 0.01 \text{ \AA}$, $b = 8.85 \pm 0.01 \text{ \AA}$, $c = 5.36 \pm 0.005 \text{ \AA}$, $\beta = 105^\circ 37' \pm 10'$, $Z = 4[\text{Ca}_{1.0}\text{Mg}_{0.30}\text{Ti}_{0.45}\text{Al}_{0.13}(\text{Al}_{0.74}\text{Si}_{1.26})\text{O}_6]$. The indices of refraction for sodium light are $\alpha = 1.747$, $\beta = 1.750$, $\gamma = 1.762$, all ± 0.005 . The color is deep green for light polarized in (100) and red perpendicular to (100). Electron microprobe analysis and optical spectra are consistent with most of the titanium being trivalent.

Least-squares refinement of 667 X-ray diffraction data (weighted $R = 0.025$) shows the structural similarity with terrestrial fassaite. The presence of titanium in the tetrahedral site is ruled out on the basis of mean bond length as well as electron density. Differences in individual bond lengths between the Allende pyroxene and diopside can be explained by electrostatic considerations and by the ionic radii.

Optical spectra show bands at $21,000 \text{ cm}^{-1}$ and $16,500 \text{ cm}^{-1}$. The $21,000 \text{ cm}^{-1}$ band is relatively weak and present for all orientations; it probably represents the crystal-field absorption of Ti^{3+} . The $16,500 \text{ cm}^{-1}$ band is strong for light with a component of vibration in (100); it probably represents charge transfer between Ti^{3+} and Ti^{4+} in $M1$ positions. Pleochroism of terrestrial titanian pyroxenes is similar in orientation to that of the Allende pyroxene, but the color is different. We suggest that the red to purple color of terrestrial pyroxenes is caused by Fe^{2+} - Ti^{4+} charge transfer, and that Ti^{3+} is not present.

Introduction

Certain chondrules or inclusions in the Allende meteorite (Clarke *et al.*, 1970) and in the Vigarano meteorite contain dark green, pleochroic pyroxene (Fuchs, 1971; Christophe-Michel-Levy *et al.*, 1970). The titanium oxide content of some of these pyroxenes has been found by electron microprobe analysis to be over fifteen wt percent (as TiO_2). This titanium content is much higher than any previously reported in natural pyroxenes, and so the details of the crystal chemistry of one of these pyroxenes should be helpful to an understanding of the role of titanium in pyroxenes and silicates in general. We have, therefore, carried out refinement of X-ray diffraction data for a crystal of Allende pyroxene, and have also obtained visible-region absorption spectra.

We shall refer to this pyroxene as a titanian fassaite because of its chemical and structural similarities with more usual terrestrial fassaite; these similarities will be set forth in more detail below.

Occurrence and Chemical Data

Materials for this study were crystals picked from a large (1 cm diameter) chondrule and a polished thin section of the same chondrule (USNM 3848). This chondrule is of the type gehlenite-fassaite-anorthite-spinel (type IIa) of Clarke *et al.* (1970), although anorthite seems to be absent from this particular specimen. The pyroxene crystals range in size from less than 0.05 mm to over 1 mm in diameter. They are generally surrounded by gehlenite, and the smaller crystals of pyroxene are sprinkled as inclusions throughout grains of gehlenite. The large pyroxene crystals seem as a rule to contain one or more large grains of dark-red rhönite (Fuchs, 1971), and surrounding many of the larger crystals is what appears to be a reaction rim of as yet unidentified material. The main part of most of the pyroxene grains, however, is essentially unaltered.

A microprobe analysis, the average for several grains in the section, is given in Table 1. A noteworthy point is the lack of iron; it was below the limit of detection (0.03 percent) in the pyroxene from this chondrule.

It is not generally feasible, of course, to distinguish between the quadri- and trivalent states of titanium by means of the microprobe. In this case the analyst

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TABLE 1. Electron Microprobe Analysis of Titanian Fassaite from the Allende Meteorite

Oxide	Wt. %	Cations per six oxygen anions
SiO ₂	32.8	1.26
TiO ₂	4.7 *	0.14
Ti ₂ O ₃	10.7 *	0.34
Al ₂ O ₃	19.3	0.87
CaO	24.6	1.01
MgO	6.7	0.38
Σ	98.8	4.00

*Total titanium, which equals 16.6% as TiO₂, has been partitioned between Ti³⁺ and Ti⁴⁺ in order to make the cations total to exactly 4.00. Analyst, J. Nelen, U. S. National Museum. Chromium was not looked for, but Fuchs (1971) found none in a similar specimen.

reported all titanium as TiO₂, 16.6 percent. However, when the structural formula is calculated from the chemical data, assuming that all titanium is Ti⁴⁺, an insufficient number of cations is obtained, 3.88 per six oxygen atoms, whereas the stoichiometric structure requires 4.00 cations. This is a fairly sizable discrepancy. Fuchs (1971) has pointed out comparable or larger discrepancies in previous analyses of Allende and Vigarano pyroxenes. If we assume that the specimen is stoichiometric, we can partition the titanium between Ti³⁺ and Ti⁴⁺ as shown in Table 1. This indicates that about 70 percent of the titanium is trivalent. Although this type of calculation is not completely conclusive, it does constitute a strong indication, independent of the spectral considerations discussed below, that a substantial amount of Ti³⁺ is present.

Since iron and other elements with variable valence are absent, it might well be possible to ascertain the Ti³⁺/Ti⁴⁺ ratio by a standard titrimetric determination of total reducing capacity. Unfortunately, there is far too little material available at present for any wet-chemical determinations.

The chemical characteristics of terrestrial fassaite are the presence of essentially the maximum amount (one atom per six oxygen atoms) of calcium and substantial quantities of the trivalent cations, aluminum and ferric iron. The Allende pyroxene fits this description well, if we take titanium, most of which is probably trivalent, in place of ferric iron.

X-Ray Refinement

An X-ray refinement of the crystal structure was carried out on the Allende pyroxene for two reasons:

first, to ascertain if there was any possibility of titanium assuming tetrahedral coordination in replacement of silicon, as has often been advocated in the past for terrestrial pyroxenes; and, second, to verify that the structure was essentially that of normal, low-titanium pyroxenes (*i.e.*, diopside structure) and to determine in particular whether the presence of so much titanium and aluminum causes any unusual configurations in any part of the structure. Our preliminary X-ray photographic work with standard precession methods showed that the space group of the Allende pyroxene is *C2/c*, the same as that of diopside.

Experimental details. The cell constants (Table 2) were obtained from quartz-calibrated precession film measurements. The crystal used for data collection was an irregular fragment less than 0.1 mm in maximum dimension and was mounted with [010] along the ϕ -axis of the Picker single-crystal diffractometer. Zr-filtered Mo radiation was used; the data collection and refinement procedures were essentially those given by Clark *et al.* (1969). A total of 865 data were collected; of these 667 had net intensities greater than four standard deviations of the background based on counting statistics and were included in the refinement. Computer programs RFINE and BADTEA, written by Dr. L. W. Finger, Geophysical Laboratory, Washington, D. C., were used throughout the refinement. The weighting scheme described by Clark *et al.* (1969) was applied and statistical weights were used in the final refinement. No corrections for absorption ($\mu = 26.8 \text{ cm}^{-1}$) or for secondary extinction were made. No reflections appeared to be affected by primary extinction.

The initial site-occupancies were taken from the calculated formula in Table 1. It seems clear from the analysis that calcium fills the M2 site; thus the only uncertain quantity in the site occupancies was the distribution of titanium and aluminum between

TABLE 2. Cell Parameters, Atomic Coordinates, Site Occupancies, and Isotropic Temperature Factors for the Allende Pyroxene*

Atom	Assumed site occupancy	Parameter			
		x	y	z	B(Å ²)
T	0.365 Al, 0.645 Si	0.2882(1)**	0.0934(1)	0.2260(2)	0.45(2)
O(1)	1.0	0.1119(2)	0.0872(2)	0.1352(4)	0.64(4)
O(2)	1.0	0.3634(2)	0.2569(2)	0.3214(4)	0.86(4)
O(3)	1.0	0.3524(2)	0.0198(2)	-0.0105(4)	0.67(3)
M(1)	0.39 Mg, 0.48 Ti, 0.13 Al	0.	0.9067(1)	0.2500	0.62(2)
M(2)	1.00 Ca	0.	0.3078(1)	0.2500	0.77(2)

*Monoclinic, $a = 9.80 \pm 0.01$, $b = 8.85 \pm 0.01$, $c = 5.36 \pm 0.01$ Å, $\beta = 105^\circ 37' \pm 10''$

$Z = 4[\text{Ca}_{1.00}\text{Mg}_{0.39}\text{Ti}_{0.35}\text{Ti}_{0.13}\text{Al}_{0.13}(\text{Al}_{0.74}\text{Si}_{1.26})\text{O}_6]$

**Error in parentheses is one standard deviation in terms of last decimal place cited. Thus 0.2882(1) and 0.45(2) respectively represent standard deviations of 0.0001 and 0.02.

TABLE 3a. Anisotropic Temperature Factor Tensor Values for the Allende Pyroxene*

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
T	12.6(7)	13.6(8)	48(4)	0.3(7)	10(1)	-2(1)
O(1)	22(2)	23(2)	47(10)	1(2)	16(3)	-2(3)
O(2)	32(2)	25(2)	63(11)	3(2)	16(4)	2(4)
O(3)	16(2)	25(2)	62(9)	3(2)	9(3)	-7(4)
M(1)	16.0(9)	20(1)	63(5)	0	8(1)	0
M(2)	26.3(8)	20.4(8)	61(4)	0	5(1)	0

* $\beta_{ij} \times 10^4$; temperature factor form, $\exp \left\{ -\sum_{i=1}^3 \sum_{j=1}^3 h_i h_j \beta_{ij} \right\}$.

For M(1) and M(2), $\beta_{12} = \beta_{23} = 0$. Error in parentheses is one standard deviation.

the M1 and tetrahedral sites. It was assumed that the presence of titanium in the tetrahedral site could be detected from the bond distances and temperature factor, and occupancies were not refined. Starting values for positional and thermal parameters were taken from the refinement of fassaite reported by Peacor (1967). Refinement with isotropic temperature factors converged in two cycles to a weighted R factor of 0.029 ($R_{wt.} = [\sum w(|F_o| - |F_c|)^2 / \sum w F_o^2]^{1/2}$). Addition of anisotropic temperature factors reduced the weighted R to 0.025 in three more cycles. Final parameters are given in Tables 2 and 3, and observed and calculated structure factors are compared in Table 4³.

Discussion of the Structure

The final parameters from X-ray refinement are similar to those found for a terrestrial fassaite (Peacor, 1967). Actually, the terrestrial fassaite in many respects represents an intermediate case between diopside (Clark *et al.*, 1969) and the Allende fassaite. The mean bond lengths for the tetrahedral, M1, and M2 sites (Table 5) of the Allende fassaite can be largely rationalized on the basis of known ionic radii, and tend to support for the most part the chemical formula which was assumed for the refinement.

The mean tetrahedral cation-oxygen distance observed, 1.677 Å, is very close to the value of 1.682 Å calculated from the assumed formula, using the effective ionic radii of Shannon and Prewitt (1969). The temperature factor of the tetrahedral site in the Allende pyroxene seems perfectly normal, and there is thus no evidence for the presence of cations other

than silicon and aluminum in tetrahedral coordination. Were there any titanium in the tetrahedral site, we would expect the temperature factor to be abnormal and the R factor to be higher.

The mean M1-O distance, 2.059 Å (Table 5), is a little smaller than that for M1 in diopside, 2.077 Å (Clark *et al.*, 1969). A larger difference would be expected from consideration of the chemical formula and the effective ionic radii (Shannon and Prewitt, 1969) for Ti³⁺ (0.67 Å), Mg (0.72 Å), and Al (0.48 Å). The discrepancy is even greater if much of the titanium is assumed to be quadrivalent, as the effective ionic radius of Ti⁴⁺ is 0.605 Å. However, the difference can be explained by taking into account the electrostatic balance of each oxygen atom, as discussed below. In any case the observed M1-O distance is more difficult to explain if it is assumed that most or all of the titanium is quadrivalent.

The mean bond length for the M2 site, 2.500 Å (Table 5) is essentially identical to that of the M2 site in diopside, 2.498 Å, in agreement with occupation of the M2 site of the Allende pyroxene entirely by calcium.

Using the principles established by Pauling (1929), the sum of the bond strengths to an atom, if not exactly equal to the formal valence of the atom, may be related to the deviation of bond lengths from

TABLE 3b. Magnitudes and Orientations of Thermal Ellipsoids for the Allende Pyroxene*

Atom	Axis i	RMS amplitude (Å)	Angle (°) of r_i with		
			a	b	c
T	1	0.067(3)	140(12)	63(15)	50(9)
	2	0.074(2)	119(15)	150(15)	80(13)
	3	0.083(3)	66(10)	102(12)	41(9)
O(1)	1	0.070(9)	121(8)	80(10)	18(10)
	2	0.096(5)	101(29)	21(30)	104(12)
	3	0.103(4)	33(13)	71(32)	78(12)
O(2)	1	0.090(9)	106(10)	91(26)	2(17)
	2	0.099(5)	104(12)	14(9)	89(27)
	3	0.122(4)	22(8)	76(8)	89(7)
O(3)	1	0.079(6)	144(21)	61(10)	58(22)
	2	0.089(6)	119(25)	105(18)	132(20)
	3	0.107(5)	109(9)	147(10)	59(12)
M(1)	1	0.085(2)	15(16)	90	90(16)
	2	0.088(2)	90	180	90
	3	0.093(4)	106(15)	90	0(16)
M(2)	1	0.089(3)	77(4)	90	28(4)
	2	0.090(2)	90	180	90
	3	0.114(2)	167(4)	90	61(4)

Error in parentheses is one standard deviation.

³Table 4 may be ordered as NAPS Document No. 02025 from Microfiche Publications, Division of Microfiche Systems Corporation, 305 East 46th Street, New York, N. Y. 10017, remitting in advance \$1.50 for microfiche or \$5.00 for photocopies. Please check the latest issue of this journal for the current address and prices.

their expected or mean values. We show here in a qualitative way how the length of the bonds is affected by electrostatic considerations of this sort.

The sums of the ionic bond strengths for the three oxygen atoms in diopside and in the hypothetical end-member pyroxenes CaTi³⁺AlSiO₆ and CaTi⁴⁺Al₂O₆ are compared in Table 6. By taking into account the bond distances in diopside, following the method suggested by Zachariasen (1963), Clark *et al.* (1969) showed that the sums come close to the actual ionic charge. However, the simple ionic model used in calculating the values in Table 6 yields sizable imbalances if bond distances are ignored. The O1 atom in CaTi³⁺AlSiO₆ receives a greater positive charge than the O1 atom in diopside, while for the O3 atom the reverse is true; the charge received by the O2 atom does not change very much. Thus in CaTi³⁺AlSiO₆, the O1 atom is assumed to have less negative character, and the bonds to it from a given cation should tend to be longer than those to the other oxygen atoms when compared to diopside, after differences in ionic radii are taken into account. That is to say, if each bond

TABLE 6. Comparison of Ionic Bond Strengths for Diopside and Two End-Member Titanian Pyroxenes

Oxygen atom	Associated cation	Bond strengths* (valence units)		
		CaMgSi ₂ O ₆	CaTi ³⁺ AlSiO ₆	CaTi ⁴⁺ Al ₂ O ₆
O(1)	T	1.000	0.875	0.750
	M(1)	0.333	0.500	0.667
	M(1)	0.333	0.500	0.667
	M(2)	0.250	0.250	0.250
	Σ =	<u>1.917</u>	<u>2.125</u>	<u>2.334</u>
O(2)	T	1.000	0.875	0.750
	M(1)	0.333	0.500	0.667
	M(2)	0.250	0.250	0.250
	Σ =	<u>1.583</u>	<u>1.625</u>	<u>1.667</u>
	O(3)	T	1.000	0.875
T		1.000	0.875	0.750
M(2)		0.250	0.250	0.250
M(2)		0.250	0.250	0.250
Σ =		<u>2.500</u>	<u>2.250</u>	<u>2.000</u>

*The ionic bond strength for an atom follows Pauling (1929) and is its formal charge divided by the coordination number.

TABLE 5. Bond Distances Compared for the Allende Pyroxene and Diopside

Atoms ^a	Distance (Å)		Difference (Å)
	Allende pyroxene ^b	Diopside ^c	
Si-O1A	1.666	1.602	+0.064
Si-O2A	1.642	1.585	+0.057
mean, nonbrg.	<u>1.654</u>	<u>1.594</u>	
Si-O3A1	1.690	1.664	+0.026
Si-O3A2	1.709	1.687	+0.022
mean, brg.	<u>1.700</u>	<u>1.676</u>	
mean of 4	<u>1.677</u>	<u>1.634</u>	
M1-O1A1, B1	2.120	2.115	+0.005
M1-O1A2, B2	2.064	2.065	-0.001
M1-O2C1, D1	1.993	2.050	-0.057
mean of 6	<u>2.059</u>	<u>2.077</u>	
M2-O1A1, B1	2.399	2.360	+0.039
M2-O2C2, D2	2.399	2.353	+0.046
M2-O3C1, D1	2.546	2.561	-0.015
M2-O3C2, D2	2.658	2.717	-0.059
mean of 6	<u>2.448</u>	<u>2.425</u>	
mean of 8	<u>2.500</u>	<u>2.498</u>	

^aAtom designations according to the nomenclature by Burnham *et al.* (1967); brg. = bridging.

^bOne standard deviation, ±0.002 Å.

^cData from Clark *et al.* (1969).

length in diopside is subtracted from its equivalent in CaTi³⁺AlSiO₆, the difference should be more positive for those bonds involving O1 than for those involving O2, and more positive for O2 than for O3. Similar predictions apply also to the hypothetical pyroxene CaTi⁴⁺Al₂O₆, for which the differences should be even more pronounced. The actual changes, shown in Table 5, are largely in accordance with this analysis. The correspondence is not exact, and bond type (covalency) may have some effect on the bond lengths, but so might the electrostatic effects of second-nearest neighbors, which were not taken into account in the predictions.

The cations in both the tetrahedral and the M2 site are coordinated by all three crystallographically distinct oxygen atoms, whereas M1 is coordinated by O1 and O2 atoms only. Thus for the tetrahedral and M2 sites, the expected changes come close to balancing out, with possibly a slight negative change in mean bond length being expected. But for M1 a net positive character is expected, and in fact the observed mean bond length is somewhat larger than that which would be calculated from the sum of the ionic radii.

Despite the differences in individual bond lengths from those of diopside, we conclude that the structure of the Allende pyroxene is essentially the same, and in particular that the coordination of titanium in M1 is not substantially different from that of magnesium in M1 of diopside. We can probably also conclude from the success of the refinement that the Allende pyroxene is stoichiometric, contrary to the suggestion of Fuchs (1971).

The normal (110) cleavage was not observed in the Allende pyroxene, either in thin section or in fragments. This is very likely related to the substitution of aluminum for silicon in the tetrahedral site, which tends to weaken the silicate chain bonds, and the substitution of titanium and aluminum for magnesium in the *M1* site, which tends to strengthen the bonds which link the chains to each other. Thus the strongly heterogeneous bonding which leads to a structure dominated by the chains is disrupted, and the cleavage which is based on these chains is suppressed.

Optical Properties

In thin section, the Allende fassaite is dark green, pleochroic to brownish red. This relatively intense color is in itself highly suggestive that a reduced state of titanium is present. Titanium is the only transition element present in more than trace quantities, and its quadrivalent state is not expected to give a strong color by itself. The green color is actually similar to that of a synthetic pyroxene, $\text{NaTi}^{3+}\text{Si}_2\text{O}_6$, reported by Prewitt *et al.* (1972), for which the valence state of the titanium is undoubted because of the total chemistry of the pyroxene. The correspondence in color with that of the synthetic pyroxene is even more strongly indicative of a reduced state for part of the titanium in the Allende pyroxene.

In order to determine in more detail how the color, pleochroism and other optical properties may be related to the valence state of the titanium ions, we have obtained polarized visible-region absorption spectra of the Allende fassaite, and have made microscope measurements of the optical properties of single grains using spindle stage methods.

Experimental methods. The optical spectra were taken on a Perkin-Elmer double-beam spectrophotometer fitted with a polarizing microscope in the sample beam. The optical orientations of all large grains in the thin section were first determined on a universal stage. Spectra were then taken of the most suitably oriented grains with the spectrophotometer. Since the crystals were far from perfect, all being more or less cracked, and precise orientations were impossible to attain on the flat stage of the spectrophotometer, the spectra are only qualitative. In particular, the precise absolute absorption and relative absorption for the different orientations could not be ascertained, because of internal reflection from the cracks. However, the spectra should suffice for the purposes of the present report.

Optical orientation was measured using standard conoscopic microscope techniques. Because cleavage or other morphology is rare and was not observed at all in the thin section, a special spindle stage, adapted for single crystals

mounted on an X-ray goniometer head⁴, was used. The crystallographic orientation was first established by X-ray precession photography, and then the optical orientation was determined on the special spindle stage. The indices of refraction were determined by the immersion method at room temperature.

The experimental methods described here are, of course, not those which would ideally be used to obtain a complete optical characterization of a mineral. They are necessitated, however, by the nature of the material—for example, we were able to separate no more than 8 mg of pyroxene from the meteorite, in the form of fragments all smaller than 0.5 mm diameter.

Results

Absorption spectra. The polarized absorption spectra of the Allende fassaite in the visible region (Fig. 1a) show three principal features: (1) a band at $16,500\text{ cm}^{-1}$, whose intensity varies with orientation; (2) a weaker band at about $21,000\text{ cm}^{-1}$; and (3) a sloping background absorption, the absorption edge, which presumably extends into the visible from an intense absorption in the ultraviolet.

The spectra in Figure 1a establish the number and locations of the features which cause the colors observed in the pyroxene. However, these spectra are not adequate to describe the polarizations of the absorption bands, for several reasons: (a) the poor quality of the crystals tends to reduce the variations in intensity due to polarization; (b) the limited number of crystals of measurable size in the section makes it unlikely that all the necessary crystallographic orientations could be attained on our flat-stage instrument; (c) the precise crystallographic orientation in the (010) plane, which as explained below is the most critical aspect of the polarization of the $16,500\text{ cm}^{-1}$ band, cannot be ascertained on the crystals in the thin section, because they apparently lack cleavage or other morphology. It is necessary to use spindle-stage techniques in order to ascertain the precise nature of the polarization.

The Allende pyroxene displays a variation in color from deep green to red in polarized light. In view of the obvious variation in intensity of the $16,500\text{ cm}^{-1}$ band shown in the spectra of Figure 1a, the explanation for this pleochroism is as follows: For orientations which show a green color, absorption by the $16,500$ band is strong and thus favors transmission of light through a band in the green between the $16,500\text{ cm}^{-1}$ band and the absorption in the

⁴ A similar spindle stage is now available commercially from Charles Supper, Inc.

blue caused by either or both the 21,000 cm^{-1} band and/or the absorption edge. For orientations which show a red color, the absorption at 16,500 cm^{-1} must be weak or absent, allowing the transmission of light through the red part of the spectrum.

Observations with the spindle stage, the crystallographic orientation being ascertained by X-ray precession photography, show that the color for light with electric vibration direction polarized parallel to the *b* axis (or optic direction *Y*) is deep green. The same is true for light polarized parallel to the crystallographic *c* axis. However, as the perpendicular to the (100) plane (or the *a** axis) is approached from any direction, the color becomes brownish and then essentially pure red. The orientation which gives the purest red color definitely does not coincide with the optic *X* or *Z* directions measured in yellow light (see below). We take these observations as clear evidence that the 16,500 cm^{-1} band is strong for light with a major component of vibration in the crystallographic plane (100), but weak or absent for light vibrating solely in the perpendicular to (100). For the reasons given above, the spectra shown in Figure 1a coincide only approximately with these polarization directions, and are not expected to show the full range of intensity of the 16,500 cm^{-1} band. In particular, the exact perpendicular to (100) is difficult to locate, and therefore some absorption by the 16,500 cm^{-1} band is difficult to avoid.

There is no evidence that the 21,000 cm^{-1} band or the absorption edge are appreciably polarized. No variation in their intensity is apparent in Figure 1a, and all the colors observed, red through green, require some absorption in the blue part of the spectrum.

Optical orientation. The optic orientation of the Allende pyroxene in yellow light, or white light neglecting anomalous dispersion, seems to be similar to that of diopside. Measurements on the spindle stage with a sodium D (yellow) interference filter yield $Z \wedge c = 58^\circ$, $b = Y$, indices of refraction $\alpha = 1.747$, $\beta = 1.750$, $\gamma = 1.762$ (all ± 0.005) and $2V (+) = 64^\circ$ for the crystal used in the X-ray refinement.⁵ (Fig. 2). However, several optical effects are present which demonstrate the existence of strong inclined dispersion. (a) In white light, the purest red color (absence of green) is observed for

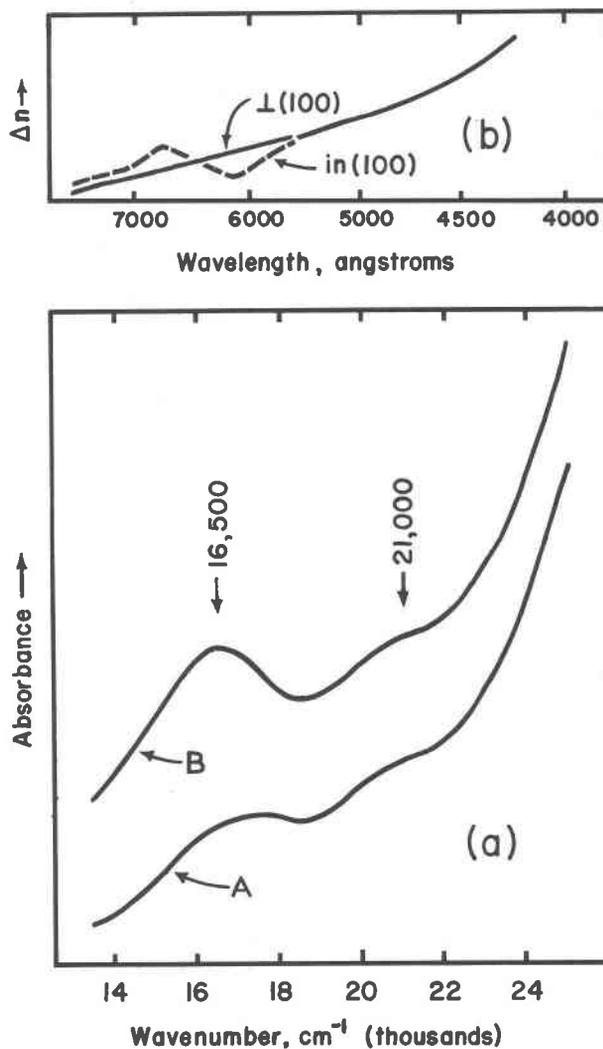


FIG. 1. (a) Polarized optical absorption spectra of the Allende fassaite. Spectrum A is for a direction showing brownish-red color, near the perpendicular to (100). Spectrum B is for a direction showing green color, near the crystallographic *c* axis. Vertical displacement of the two spectra is arbitrary. (b) Schematic diagram of the changes in refractive index to be expected from the observed absorptions, with respect to a pyroxene in which these absorptions are absent. This diagram assumes that the intense absorption in the ultraviolet which produces the absorption edge is not polarized (see text).

light vibrating perpendicular to (100), rather than in either the *X* or *Z* optic directions measured in yellow light. (b) The interference figure for one of the optic axes, *B* in Figure 2, is anomalous; the isogyre perpendicular to the optic plane is pure red. This indicates a different $2V$ for red light. It was not even possible to locate an isogyre complementary in color to the observed red one which would

⁵ The angle $2V$ for two other grains measured on the spindle stage was about 80° .

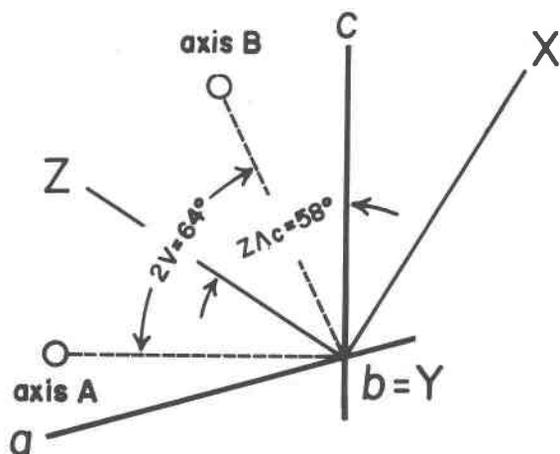


FIG. 2. Optical orientation in sodium D light of the Allende fassaite.

represent optic axis *B* for red light. The other optic axis, *A*, gives an apparently normal interference figure. (c) Anomalous interference colors are observed. If the view direction (microscopic axis) is perpendicular to the optic *Y* direction, extinction is normal and black, but as the view direction approaches *Y*, extinction is not complete, and the crystal is alternately red and deep violet as it is rotated through the extinction position.

Discussion

(1) *The band at 16,500 cm⁻¹.* From the observed polarization of this band, it is obvious that

it must be caused by some kind of interaction taking place primarily in the (100) plane. This can be explained only on the basis of a direct cation-cation, intervalence charge-transfer interaction (Allen and Hush, 1967; Hush, 1967; Linnehan and White, 1971), as shown by the following analysis.

In clinopyroxene, the metal sites lie in planes parallel to (100), as shown in Figure 3. The Allende fassaite apparently has its *M2* site completely filled by calcium, so we restrict our attention for the moment to the *M1* positions; these form edge-sharing zigzag chains parallel to the *c* axis (Figure 3). Direct cation-cation charge-transfer absorption can take place only when the electric vibration direction of the incident light has a component in the metal-metal vector. There are two *M1-M1* vectors (zig and zag of the *M1* chains) in the clinopyroxene structure. These lie in (100) and make angles of about 32° on opposite sides of the *c* axis. Thus, charge transfer is allowed for light vibrating anywhere in (100), although it may be slightly stronger parallel to *c* than parallel to *b*, but charge transfer is *not* allowed for light vibrating perpendicular to (100). This explains the observed polarization of the band at 16,500 cm⁻¹.

If we assume that only transition-metal cations give rise to the type of charge transfer under discussion, the only possibilities for the ions between which the transfer could take place are the different

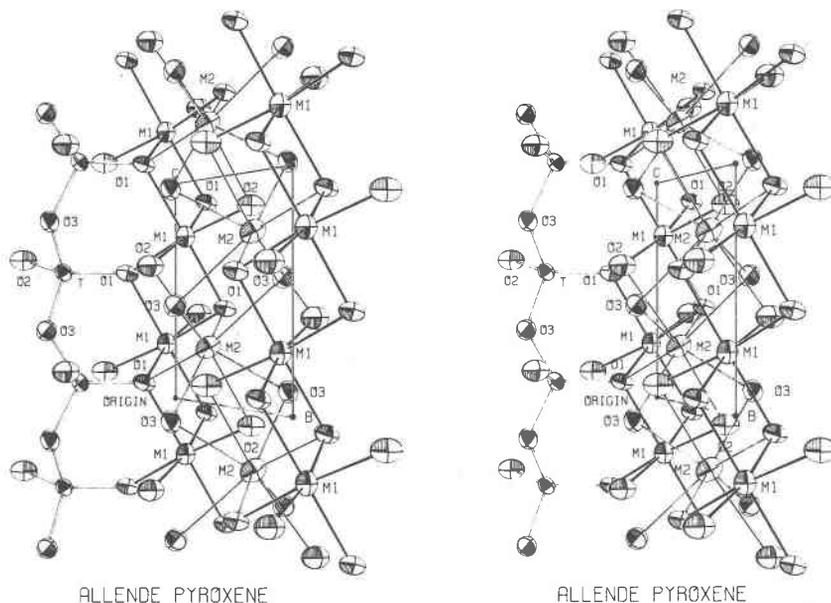


FIG. 3. Stereographic-pair view showing a slice of the structure of the Allende fassaite parallel to (100). Thermal ellipsoids are drawn with 95 percent probability distribution. Drawing produced by ORTEP (Johnson, 1970).

valence stages of titanium. Therefore, we assign the 16,500 cm⁻¹ band to Ti³⁺-Ti⁴⁺ charge transfer. This band is located approximately where presumed charge-transfer bands, mostly Fe²⁺-Fe³⁺, have been identified in pyroxenes and other silicates (Allen and Hush, 1967; Faye *et al.*, 1968; Manning and Nickel, 1969; Burns, 1970; Linnehan and White, 1971). Prewitt *et al.* (1972) have also assigned a band at 15,600 cm⁻¹ in diffuse reflectance spectra of NaTi³⁺Si₂O₆ to Ti³⁺-Ti⁴⁺ charge transfer (Ti⁴⁺ was assumed to be an impurity).

Assignment of the 16,500 cm⁻¹ band to a crystal-field absorption can be ruled out, because of its polarization. Polarization of crystal-field absorptions is due to the selection rules of the pseudo- or actual point symmetry of the site. The only ion which would give rise to a crystal-field absorption in the Allende fassaite is, of course, Ti³⁺ in the *M1* site, since this is the only ion present which has a *d* electron. The *M1* site has actual symmetry 2 (*C*₂), with the two-fold axis parallel to crystallographic *b*. This symmetry could not account for the polarization, because its selection rules do not distinguish between directions in the plane perpendicular to the two-fold axis, whereas it is just in this plane (the (010) plane) in which the polarization is most pronounced. Furthermore there is no possible pseudosymmetry of the *M1* site which could account for the polarization. Given the location of the *M1* ligands shown in Figure 3, there are no additional symmetry elements possible which come near to coinciding with the crystallographic *c* axis (which is one of the observed polarization directions), except one of the three-fold axes of the *M1* coordination octahedron. However, if the selection rules for the latter symmetry were operative, all directions perpendicular to the pseudo-three-fold axis would be equivalent, and no large difference in absorption would be predicted between the perpendicular to (100) and the *b* axis, contrary to observation.

Similar arguments apply to the possibility of the 16,500 cm⁻¹ band being due to a cation-anion charge-transfer interaction. Such an absorption would not be polarized with respect to (100), because no *M1* ligands lie in or near this plane.

(2) *The band at 21,000 cm⁻¹.* The band at 21,000 cm⁻¹ is most reasonably assigned to the crystal-field transition of Ti³⁺ in octahedral coordination. A band at about this location has been observed in the octahedral aqueous Ti³⁺ complex (Cotton and Wilkinson, 1962) and in many Ti³⁺

compounds. A band at about this location in terrestrial pyroxenes has also been attributed to the crystal-field absorption of Ti³⁺ (Chesnokov, 1959; Burns, 1970; Manning and Nickel, 1969), but there is considerable doubt about this, as will be shown below.

(3) *The absorption edge.* Since pyroxenes which do not contain transition elements normally do not have an absorption edge impinging on the visible, it is probable that the absorption edge exhibited by the Allende pyroxene is due to charge-transfer interaction primarily in the ultraviolet between titanium cations, trivalent and/or quadrivalent, and oxygen anions. Such absorption edges are common features of transition metal oxides.

Inclined dispersion. Anomalous dispersion effects, including dispersion of the optic directions and axes, may usually be attributed to differences in refractive index caused by strong absorptions. The effect of an intense absorption on refractive index is well known in classical optics (*e.g.*, Strong, 1958). Thus, as the absorption band is approached from lower frequencies, the refractive index increases, and as it is approached from higher frequencies, the refractive index decreases. There is a sharply inflected section connecting these two trends, and at the exact center of the absorption there is no change in refractive index. This behavior is illustrated in Figure 1b, using as an example of the strong absorption the 16,500 cm⁻¹ band in (100). Dispersion of optic directions or axes results when the absorption is not isotropic, and the changes in refractive index for various crystallographic directions are different.

In order to decide what kind of absorption could be causing these effects in the Allende pyroxene, it is helpful to know how the orientation of the absorption, *i.e.*, its polarization, could affect the dispersion properties. In the following analysis, we will show that the geometric nature of the dispersion effects is consistent with their being caused by an absorption in the (100) plane.

Schematic cross sections in the (010) plane of the optical indicatrix of the Allende pyroxene are shown in Figure 4. The solid ellipse represents the orientation for yellow (sodium D) light, and is what we expect at any frequency at which there are no differential effects on refractive index due to strong absorption. The dashed ellipse is intended to represent the orientation for a strongly absorbed frequency, on the high-frequency side of the 16,500 cm⁻¹ peak (say about 17,000 cm⁻¹, or 6100 Å).

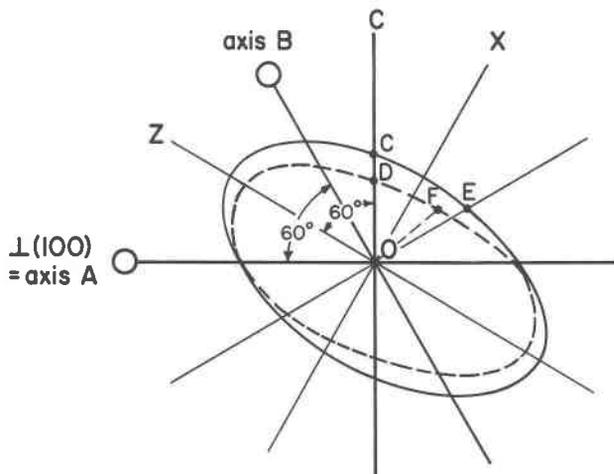


FIG. 4. Schematic diagram of a cross-section in (010) of the optical indicatrix of the Allende fassaite. Solid ellipse is for a frequency unaffected by absorption; dashed ellipse is for a frequency affected by a strong absorption polarized in (100). The ellipticity of the indicatrix and its modification by absorption are greatly exaggerated.

Although the optics for very strongly absorbing crystals are complex, involving elliptical polarization and other effects, we assume that such complications can be neglected to a first approximation, and that the optical orientation for the absorbed frequency can be derived from the expected changes in refractive index shown in Figure 1b. At the frequency in question, the refractive index is decreased in (100), as shown by the dashed line in Figure 1b, but unchanged in the perpendicular to (100) (relative to the overall change which is shown by the solid line). In Figure 4, the decrease in refractive index in (100) is represented by the difference in length between line segments OC and OD. The dashed ellipse is passed through D, and drawn in such a way that the difference between it and the solid ellipse decreases to zero at the perpendicular to (100). Note that the principal axes of the dashed ellipse, and therefore the optic X and Y directions, are different from those for the solid ellipse.

We call particular attention to the behavior of the optic axes A and B. Assuming that the optic Y direction always corresponds to crystallographic *b*, optic axes A and B for yellow light are perpendicular to ellipse radii OC and OE, where OC and OE correspond in length to the refractive index β . For the strongly absorbed light to which the dashed ellipse pertains, we have already stated that the index in (100) is now given by OD, and since β is in (100)

it is also represented by OD and OF. Due to the changed size and orientation of the dashed ellipse, radius OF does not coincide with radius OE of the solid ellipse. Thus, although optic axis A remains unchanged in position for the two frequencies represented by solid and dashed ellipses, optic axis B, which is perpendicular to OF, is closer to optic axis A for the absorbed frequency.

A similar analysis may be applied to frequencies slightly lower than the absorption peak. In this case, optic axis A retains the same orientation, as above, but the indicatrix is rotated in the opposite direction, and $2V$ is increased.

Clearly, this interpretation explains the observation that optic axis A in the Allende pyroxene is essentially normal while axis B is notably dispersed. It would be difficult to explain this observation on any other basis than an absorption polarized in (100), and the $\text{Ti}^{3+}\text{-Ti}^{4+}$ charge-transfer band at $16,500\text{ cm}^{-1}$ is the obvious candidate for this absorption. The absorption would not be quite the same parallel to *b* as to *a*, as required by the above analysis, but the difference would probably not be sufficient to cause appreciable dispersion of optic axis A. Some calculations made by W. T. Holser (personal communication) indicate that changes in refractive index to be expected from an absorption of the strength of the $16,500\text{ cm}^{-1}$ band are small, on the order of 0.001. However, this may be adequate to cause dispersion of the optic axis B sufficient to account for the observations, considering that the birefringence is 0.015. An important point in the above interpretation is that for the affected frequencies, optic axis B would be dispersed in both directions from its position in the unaffected frequencies.

Another hypothesis which must be considered is that the inclined dispersion arises from the strong absorption, or absorptions, in the ultraviolet which cause the absorption edge. In this case we would be seeing only the effect which occurs on the low frequency side of the absorption. Although the strongest part of the absorption edge does not extend far into the visible, its dispersion effects would be manifest at much lower frequencies. The inclined dispersion would be a result of the refractive index curves for different crystallographic directions having different slopes through the visible, because of polarization of the absorption in the ultraviolet. Inclined and crossed dispersion in many compounds are attributable to effects of this kind.

In our case, however, there are two objections to

the hypothesis. The first is the polarization—it is difficult to see why such an absorption should be polarized in (100), as apparently required by the above analysis. The ultraviolet absorption is most probably a cation-anion charge transfer, and there is no particular reason why such an absorption should be polarized in (100), considering that no *M*1 ligands lie in (100). This hypothesis is only reasonable if the ultraviolet absorption is some type of direct cation-cation charge transfer between *M* site cations in (100). Other than Ti³⁺-Ti⁴⁺, which is accounted for, the possibilities seem to be rather obscure. Secondly, we have observed that it is only the red part of the spectrum which is affected by inclined dispersion; that is, the optical orientation for the spectrum from yellow to violet is not dispersed, or else we would see colors other than red in the interference figure. This is perfectly consistent with the cause of inclined dispersion being the 16,500 cm⁻¹ band, but is difficult to explain on the basis of an absorption in the the ultraviolet.

Thus the inclined dispersion seems to be most reasonably explained by the presence of the Ti³⁺-Ti⁴⁺ charge-transfer band, although the other hypothesis should probably not be completely ruled out until the polarization of the ultraviolet absorption is measured.

Oxidation State of the Allende Fassaite

The chondrules containing the Ti³⁺-fassaite are of an unusual calcium-aluminum-rich and iron-poor type found in only a few meteorites. The iron-poor nature is illustrated by the apparent lack of iron in the pyroxene, and very low iron concentration in the rhönite grains with which the pyroxene is associated; the Allende rhönite has less than 0.9 percent FeO (J. Nelen, personal communication), whereas terrestrial rhönites contain over 20 percent iron oxide (Cameron *et al.*, 1970). This near lack of iron seems to point toward a very low oxidation state, even compared to most meteorites. Of the several modes of origin proposed for the iron-poor chondrules and inclusions in Allende and other meteorites, possibly the most widely accepted at the present time is that they represent very early condensates of refractory material from the hot solar nebula (Marvin *et al.*, 1970). This hypothesis implies a low oxidation state during formation because the partial pressure of hydrogen in the nebula would still be relatively high at this early stage. In order to explain the low iron concentration in these

chondrules and inclusion, other proposed modes of origin (Kurat, 1970; Keil and Fuchs, 1971) apparently must rely either on nearly complete reduction of the iron to the metallic state, as in enstatite chondrites and achondrites (Mason, 1966), or on extreme volatilization. The latter probably implies reduction as well, because oxygen loss would very likely be greater than iron loss.

In any case, it seems clear that the oxidation state of the Allende fassaite is much lower than that of terrestrial titanian pyroxenes, which contain Fe³⁺, and probably also lower than that of lunar pyroxenes, which contain substantial amounts of Fe²⁺.

Terrestrial and Lunar Titanian Pyroxenes

The red-violet color of terrestrial titanian augites has very often in the past been attributed to the presence of Ti³⁺. The color is actually caused by a broad absorption band at 19-22,000 cm⁻¹, a band that has been assigned to the crystal-field transition of Ti³⁺ (Chesnokov, 1959; Burns, 1970; Manning and Nickel, 1969). We have made the same assignment for the band at 21,000 cm⁻¹ in the Allende pyroxene, but there are some very important differences in the properties of terrestrial titanian pyroxenes versus the Allende fassaite.

Firstly, in terrestrial titanian pyroxenes, the 19-22,000 cm⁻¹ band and accompanying red-violet color can be very strong, despite a relatively small amount of titanium present. Titanium oxide in terrestrial pyroxenes is almost always less than 6 percent and only a fraction of this could be Ti³⁺, if Ti³⁺ is present at all. The Allende pyroxene must have a higher Ti³⁺/Ti⁴⁺ ratio, as well as much higher titanium content, and shows only a moderately intense red color in the perpendicular to (100).

Secondly, terrestrial titanaugites are strongly pleochroic, and the red-violet color is usually described as being absent or weak for *Z*. However, it is likely that many investigators have not been aware of the complications discussed in this report, and in describing the pleochroic colors, have mistaken the perpendicular to (100) for *Z*. Deer *et al.* (1962, p. 133) have pointed out that "In some titanaugites the absorption indicatrix does not coincide with the optical indicatrix, and in such cases the pleochroism is more easily related to the direction of the *y* [= *b*] and *z* [= *c*] axes and the direction at right angles to the *yz* [= (100)] plane." Furthermore, inclined dispersion is the rule in terrestrial titanaugites (*e.g.*,

Dixon and Kennedy, 1933; Holzner, 1934), and its orientation seems to be analogous to that found in the Allende pyroxene. If these optical properties are due to the 19-22,000 cm^{-1} band, the conclusion must be that this band is identical in its polarization to the 16,500 cm^{-1} band in the Allende pyroxene.

Thirdly, the strong charge-transfer band at 16,500 cm^{-1} found in the Allende fassaite is not evident in terrestrial titanian pyroxenes. If appreciable Ti^{3+} were present, we might expect this band to dominate and produce a green color, since charge-transfer absorptions are generally expected to be stronger than octahedral crystal-field absorptions.

These considerations very strongly suggest that the red-violet color and pleochroism of terrestrial titanaugite are not caused by the crystal-field absorption of Ti^{3+} , but by a charge transfer similar to that found in the Allende pyroxene, involving, of course, different species. The choice of a suitable cation pair is limited, since we apparently must assume that titanium is involved, because of the general correlation of color with titanium content. We suggest that $\text{Fe}^{2+}\text{-Ti}^{4+}$ is the only pair that satisfies the requirements. This would be a heteronuclear charge transfer (Allen and Hush, 1967), very few examples of which have been reported in minerals. A blue or green color in some sapphires has been attributed to $\text{Fe}^{2+}\text{-Ti}^{4+}$ charge transfer (Townsend, 1968; Ferguson and Fielding, 1971). In this case a somewhat lower energy for the absorption (14,200 to 17,800 cm^{-1}) could be ascribed to the different structures; the sites involved in sapphire share faces, rather than edges. It is possible that some charge-transfer bands previously identified in minerals have been incorrectly assigned, and are actually due to $\text{Fe}^{2+}\text{-Ti}^{4+}$. For example, Faye and Harris (1969) showed that a band at 21,000 cm^{-1} in the spectrum of andalusite is very strongly polarized, and assigned this band to $\text{Ti}^{3+}\text{-Ti}^{4+}$ charge transfer. However, the assignment to $\text{Fe}^{2+}\text{-Ti}^{4+}$ (which Faye and Harris apparently did not consider) seems equally valid, since their andalusite specimens contained iron as well as titanium.

Most terrestrial titanian pyroxenes are salitic, and hence most Fe^{2+} , as well as Ti^{4+} , is in the $M1$ site. The $\text{Fe}^{2+}\text{-Ti}^{4+}$ charge transfer would therefore usually be similar in its polarization properties to the $\text{Ti}^{3+}\text{-Ti}^{4+}$ charge transfer in the Allende pyroxene. In some cases, however, Fe^{2+} is found in $M2$. This might allow an additional type of charge transfer slightly different from that found in the Allende fas-

saite. Charge transfer might then take place between Fe^{2+} in $M2$ and Ti^{4+} in $M1$. The shortest $M2\text{-}M1$ vector is parallel to b ($=Y$), which might lead to a slightly different color and somewhat stronger absorption parallel to b than parallel to c .

Manning and Nickel (1969) have analyzed some polarized spectra of a terrestrial titanian pyroxene, and have claimed to be able to resolve from a broad envelope the crystal-field absorption of Ti^{3+} at about 19,000 cm^{-1} , which they maintain is not polarized, and a polarized $\text{Fe}^{2+}\text{-Fe}^{3+}$ band at about 15,000 cm^{-1} . However, the thin section which they used for these measurements, cut parallel to the (001) face, was not suitably oriented for the detection of polarization of an $M1\text{-}M1$ (100) charge transfer band. The plane (001) makes an angle of about 16° with the perpendicular to (100) and this difference is probably sufficient to allow an appreciable component of an $M1\text{-}M1$ (100) charge-transfer absorption to be present in both their "polarization" directions. We therefore consider their conclusions to be questionable, especially considering that the various peaks were not visually resolvable. Their results do bring out some of the possible complications which may be present in terrestrial pyroxenes, such as $\text{Fe}^{2+}\text{-Fe}^{3+}$ charge transfer. This transfer, added to the $\text{Fe}^{2+}\text{-Ti}^{4+}$ interaction, may partly account for a variation of color in terrestrial titanaugites from red to purple or brown.

Most terrestrial fassaites contain very little titanium, but do have significant quantities of Fe^{2+} and Fe^{3+} . The $\text{Fe}^{2+}\text{-Fe}^{3+}$ charge transfer may account for the green color of many terrestrial fassaites, since it occurs at about the same frequency as the absorption causing the green color in the Allende fassaite.

To summarize, the evidence from optical spectra for the presence of Ti^{3+} in terrestrial pyroxenes seems to be extremely doubtful. Of course, there is no good reason to expect to find Ti^{3+} in terrestrial pyroxenes, since these always contain significant amounts of Fe^{3+} . Ti^{3+} is not expected to coexist with Fe^{3+} in the same mineral, and certainly not in the same site.

Lunar pyroxenes. Most lunar augites contain significant titanium (sometimes over 4 percent TiO_2) and range in color from very light pink to reddish in thin section. It has been suggested on the basis of cation balance of electron-microprobe analyses (e.g., Boyd, 1970; Hollister *et al.*, 1971; Weill *et al.*, 1971) that some of the titanium may be trivalent. It is certainly more likely that Ti^{3+} would be found in lunar

pyroxenes than terrestrial ones, since the lunar rocks contain metallic iron and no Fe³⁺. However, it does not follow that the reddish color is caused by the presence of Ti³⁺. There seems to be, in fact, a good correlation of red color with the product of the molar concentrations of titanium and iron, as we would expect if the color is caused by Fe²⁺-Ti⁴⁺ charge transfer (Dowty, in preparation).

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