

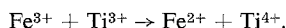
TRACE FERRIC ION IN LUNAR AND METEORITIC TITANAUGITES

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Abstract. Evidence for presence of Fe^{3+} in lunar rocks is furnished by heating them in air to 200–225°C for two hours. This causes a large decrease in the same charge transfer bands attributed to Fe^{3+} that can be enhanced by heating the same rocks in air at 500°C. This data is interpreted as evidence that the Fe^{3+} was not in equilibrium in the melt but was produced by cosmic radiation subsequent to the rock formation. The decrease of the Fe^{3+} charge-transfer bands is accompanied by decrease in intensity of spin-allowed Fe^{2+} bands attributed to M_1 sites in the pyroxene in rock 12018. This decrease in the Fe^{2+} bands is attributed to decrease in the $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+}$ charge-transfer intensification of these Fe^{2+} spin-allowed transitions when radiation-produced Fe^{3+} is partially-reduced by the low-temperature heating.

The reaction of Fe^{3+} on heating to 200–225°C is probably



This is the reverse of the reaction caused by cosmic ray bombardment of the rock on the lunar surface. Possible tetrahedrally coordinated Fe^{3+} is present in the meteoritic and lunar augites as suggested by comparison of their spectra to that of terrestrial augite high in Fe^{3+} . This would have been present in the original melt and is distinct from radiation produced Fe^{3+} in the M -sites.

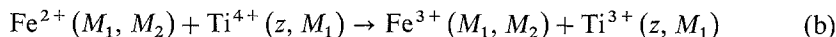
The polarized absorption spectra of single crystal pigeonite and augite from rock 12021 before heating, and augite from 12018 after heating are compared to that of meteoritic titanaugite in the Angra dos Reis meteorite and terrestrial titanaugite from Maui, Hawaii. The absorption spectrum of meteoritic hypersthene (Tatahouine) is also included for comparison to the pigeonite.

1. Introduction

It has been shown earlier (Hapke *et al.*, 1970) that heating lunar rocks at 200–225°C for 2 hr causes a large decrease in three major charge transfer bands of Fe^{3+} near 2750, 2600 and 2200 Å. This is accompanied by a decrease near 6800 Å and possibly 4675 Å of Ti^{3+} charge transfer bands (Cohen, 1972). It has been concluded that this low heating causes the reaction



to take place, indicating that the Fe^{3+} and Ti^{3+} are not in equilibrium. This led the writer to conclude that the Fe^{3+} and Ti^{3+} are produced by radiation, most likely cosmic rays (Cohen, 1972) according to the reaction



The Fe^{3+} produced would be at the M_1 and M_2 sites of Fe^{2+} , one Ti^{4+} being reduced for each Fe^{2+} oxidized. The Ti^{4+} could be at either M_1 or the $z(\text{Si}^{4+}$ tetrahedral) site. It was noted that on heating, as the Ti^{3+} decreased, the absorption in the region near the ultraviolet cut-off increased; this is attributed to increase in Ti^{4+} during oxidation of Ti^{3+} upon mild heating (Hapke *et al.*, 1970).

It was found that as Fe^{3+} charge transfer bands decreased in lunar rocks 10017, 10022 and 12018 upon heating to 200–225°C for 2 hr, bands in the Fe^{2+} region of the spectrum also decreased as shown in Table I. This was unexpected as one would expect that bands in this region would increase slightly or remain unchanged as the Fe^{3+} was reduced depending on the comparative oscillator strengths of the Fe^{3+} charge transfer bands and Fe^{2+} spin allowed d -transitions. The Fe^{2+} region showed a decrease which could only be interpreted as an interaction between the Fe^{3+} charge transfer levels and the spin allowed d levels of Fe^{2+} .

TABLE I
Effect of heating at 200–225°C on charge transfer bands of Fe^{3+} in lunar rocks

C.T. band	Rock No.	Mineral	Possible mineral site	Absorbance change
2750 A	10017,52	Augite	M_1	large decrease
	10022,48	Augite	M_1	large decrease band unresolved
2850 A	12018,50	Augite	M_1	data unavailable
2700 A	12021,65	Augite	M_1	data unavailable
2750 A	12021,65	Pigeonite	M_1	data unavailable
2250 A	10017,52	Augite	M_2	large decrease
2250 A	10022,48	{ Pigeonite Augite	M_2	large decrease
2200 A	12018,50	Augite	M_2	unresolved, prob. large decrease
2600 ^a	12017,52	Augite	z	unresolved prob. no change
2700 region	12022,48	{ Pigeonite Augite	z	unresolved
2700	12018,50	Augite	z	unresolved
Effect of heating at 200–225°C on spin-allowed d -bands of Fe^{2+} in lunar rocks				
	Rock No.	Mineral	Mineral site	
~ 10300 A	10017,52	Augite	—	decrease
~ 9900 A	10022,48	{ Pigeonite Augite	M_1	decrease
9700 A	12018,65	Augite	M_1	decrease
9050 A	12018,65	Augite	M_1	decrease

^a Cr^{3+} charge transfer band possibly also present.

In this paper the charge transfer spectral transitions of Fe^{3+} , will be given tentative structural locations based on changes during heating and other radiation effects (Hapke *et al.*, 1970). No evidence as to the nature of charge transfer has been detected, although these bands are similar to ones for Fe^{3+} in quartz (Cohen and Hassan, 1970). In Table I the probable site positions in the augite structure are given for the Fe^{3+} charge transfer bands based on the effect of mild heating.

There are three different possible sites for Fe^{3+} in the diopside structure of augite, M_1 , the major site of Mg^{2+} , M_2 , the major site of Ca^{2+} , and z , the tetrahedral Si^{4+}

site. The M_1 site is the octahedral site preferred by Fe^{3+} in the diopside structure (Hafner and Huckenholz, 1971). Fe^{3+} will also follow Al^{3+} into the z site. The Fe^{2+} ion prefers the M_2 site, will occupy the M_1 site, and cannot occupy the z site due to its size and the charge difference of +2 from Si^{4+} (Cohen and Hodge, 1958).

Since Fe^{2+} cannot occupy the tetrahedral site (this does not pertain to possible Fe^{2+} produced from Fe^{3+} by radiation-reduction but to entry into the z site as the crystal is formed from the melt) but Fe^{3+} can, heating of minerals should not affect the Fe^{3+} in this site. However Fe^{3+} produced by radiation damage by oxidation of Fe^{2+} in M_1 and M_2 sites should be reduced on heating with oxidation of an equal quantity of Ti^{3+} . Since bands at 2700–2850 Å show a large decrease upon heating to 200–225°C as do bands at 2200–2250 Å, these are likely due to Fe^{3+} at M_1 or M_2 sites. The bands at 2600–2700 Å are unresolved upon heating at 200–225°C and probably undergo no change. Charge transfer bands in this region are therefore assigned to Fe^{3+} in a tetrahedral site. Since the energy diagram of the charge transfer spectrum of Fe^{3+} has not been explored it is not known if the other two bands are two transitions at one 6-coordinate site or one each from the M_1 and M_2 site, respectively. Tentatively the 2700–2850 Å band will be assigned to an M_1 site and the 2200–2250 band to an M_2 site, until further radiation experiments can elucidate this problem. Preliminary data (Hapke *et al.*, 1970) indicates that the 2200–2500 Å band is reduced by X-ray treatment which is more likely for Fe^{3+} in an M_2 site preferred by Fe^{2+} . The same set of experiments indicates that treatment with UV light causes an increase mainly in the 2700–2850 Å band. It is expected that the oxidation of Fe^{2+} in an M_1 site would have lower activation energy than one at an M_2 site. These assignments are used later in Table IV.

The decrease in intensity of the Fe^{3+} bands is accompanied by decrease in intensity of two spin-allowed d -bands of Fe^{2+} , in rock 12018,65. These have both been assigned to the M_1 site (Cohen, 1972). The two bands assigned to the M_2 site (Cohen, 1972) show no change upon heating. The conclusion from this evidence is that only Fe^{2+} ions in sites preferred by Fe^{3+} have a charge transfer component in their spin-allowed d -transitions.

2. Experimental

The spectral data were taken using a Cary Model 14-R spectrophotometer with variable-voltage-halogen-lamp source for the visible and infrared spectral regions. Neutral density screens were used to obtain the high absorbance data in the ultra-violet region. The polarized spectra were taken using a calcite Glan prism that could be oriented to within $\pm 0.25^\circ$. Small circular matched slits were constructed in order to obtain the spectra of single crystals in the polished rock sections. The slits were individually made for each crystal investigated.

All rock sections were $\sim 30 \mu$ thick, polished on both sides and mounted on brass holders containing the fixed slits. The polished sections had no backing so the thinness was limited to 30 μ in order to handle them without breakage. With this 30 μ thickness no sections were ever broken during the experiments. All heating experiments were

performed on the thin sections without any mounting in order to avoid surface contamination. This necessitated replacement of the section in exactly the same position on the holder so that calculated difference spectra would be accurate. Replacement of minute single crystals exactly in the same position was difficult and difference spectra have as yet only been calculated using the spectrum of the whole rock, before and after radiation treatment.

Oscillator strengths of Fe^{3+} and Fe^{2+} bands in the pyroxene structure are unknown so that the Fe^{3+} concentrations are only order of magnitude estimates at best. It is considered that the total Fe^{3+} content is in the order of $0.0x\%$ by weight in the lunar rocks studied including Fe^{3+} in both tetrahedral and octahedral sites.

3. Location of Transition Cations in the Augite Structure

Electron microprobe analyses across a zoned pyroxene crystal in section 12021,2 (Dence *et al.*, 1971) show that in general as Si^{4+} , Mg^{2+} , Ca^{2+} , Al^{3+} , Ti, and Cr increase from pigeonite to augite the Fe^{2+} and Mn^{2+} decrease. From augite to pyroxferroite the trend reverses.

The lunar melt contains the $3d$ transition elements primarily in their lowest stable valence states namely Fe^{2+} ($3d^6$), Mn^{2+} ($3d^5$), Cr^{2+} ($3d^4$) and Ti^{3+} ($3d^1$). However titanium because of the stability of the unfilled $3d^0$ configuration will partially be present as Ti^{4+} . Trace quantities of Fe^{3+} (ionic radius, $r = 0.64$ Å), and Cr^{3+} (0.63) present will follow Ti^{4+} (0.68) into the tetrahedral Si^{4+} (0.42) z -position along with Al^{3+} (0.52). As the tetrahedral Si^{4+} position in α -quartz can accommodate only cations differing by a charge of ± 1 (Cohen and Hodge, 1958), it is probable that this is also the case in the diopside structure of clinopyroxenes. Therefore one would not find Mg^{2+} (0.67), Fe^{2+} (0.74), or Mn^{2+} (0.80) in the tetrahedral site even if size consideration in case of Mg^{2+} would allow it. This conclusion is contrary to a suggestion of Verhoogen that Mg^{2+} may occupy a Si^{4+} site in clinoenstatite and diopside when titanium is present (Verhoogen, 1962). Although Mg^{2+} may enter into tetrahedral coordination it is never found in the quartz structure, poor analytical data to the contrary. The ionic charge is too greatly different from the normal $+4$ in this cation position in the tetrahedral network. Thus in the lunar pyroxenes we are also undoubtedly limited to cations of $+3$ and $+4$ charge for silicon substitution in the chains of tetrahedra.

Since the original Ti^{3+} (0.76) in the lunar melt probably enters the M_1 site in augite, Al^{3+} is favored in the tetrahedral site for charge compensation. If one recalculates data (of Dence *et al.* 1971) for number of atoms present one can compare the relative Al^{3+} to Ti^{4+} and Cr^{3+} atom for atom. In their analysis number 4, for 503×10^{19} Si atoms there are 39×10^{19} Al, 9.5×10^{19} Ti and 8.0×10^{19} Cr atoms. If all the titanium were Ti^{4+} and Cr were Cr^{3+} and they occupied the M_1 site there would still be 12×10^{19} atoms of excess Al^{3+} if all went into the z site. This of course neglects possible trace Fe^{3+} in the M_1 and z sites from the original melt. Since there is Ti^{3+} and Cr^{2+} to be considered, and the Ti^{4+} that enters the z -site, it follows that there is Al^{3+}

present in the M_1 site. If trace Fe^{3+} in the melt follows the Al^{3+} it will largely be present in the z site with possibly a smaller amount in the M_1 site.

As shown in Table II the three transitions assigned to Fe^{3+} in a tetrahedral site, 4A_1 , ${}^4E(G)$, ${}^4T_2(G)$ and ${}^4T_1(G)$ (Faye and Hogarth, 1969) are present in the lunar titanauigites, 12021,65 and 12018,50. The possible presence of tetrahedral Fe^{3+} in the Angra dos Reis meteoritic titanauigite and in lunar titanauigites indicates trace Fe^{3+} may have been present in the original melt. It was expected that a portion of the Fe^{3+} present may have entered the M_1 site. However octahedral transitions of Fe^{3+} seem absent in the lunar pyroxenes (except for possible charge transfer bands). Since Ti^{4+} is low in the pigeonite one would not expect much Fe^{3+} produced by radiation to occur, and Fe^{3+} would not tend to enter the z -site in this structure.

TABLE II
Possible transitions of Fe^{3+} in tetrahedral sites

Transition	Phlogopite (Faye and Hogarth, 1969)		Orthoclase (Faye and Hogarth, 1969)		Maui, Hawaii Augite		Angra dos Reis Augite	
	A	cm ⁻¹	A	cm ⁻¹	A	cm ⁻¹	A	cm ⁻¹
${}^6A_1 \rightarrow {}^4A_1$	4405	22700	3775	26500	α 4450 β 4470	23370	α, β 4500	22225
δ cm ⁻¹		2400		2500		1670		1825
$\rightarrow {}^4T_2(G)$	4925	20300	4165	24000	α, β 4855	20600	α 4920 β 4900	20400
δ cm ⁻¹		1100		1350		1730		1370
$\rightarrow {}^4T_1(G)$	5210	19200	4415	22650	β 5300	18870	α 5210 β 5255	19030

Transition	Lunar Augite 12018,50		Lunar Augite 12021,65	
	A	cm ⁻¹	A	cm ⁻¹
${}^6A_1 \rightarrow {}^4A_1$	4550	21980	α, β 4500	22370
δ cm ⁻¹		1360		1750
$\rightarrow {}^4T_2(G)$	4850	20620	β 4850	20620
δ cm ⁻¹		1930		1750
$\rightarrow {}^4T_1(G)$	5350	18690	α 5250 β 5300	18870

4. Comparison of Spin-Forbidden Tetrahedral Bands of Fe^{3+} in Terrestrial and in Meteoritic Titanauigite with those in Titanauigite in Rocks 12021,65 and 12018,50

Rock section 12021,65 is a coarse-grained porphyritic gabbro from Oceanus Procellarum and has zoned pyroxene phenocrysts as the major mineral. The complex nature of the pigeonite-augite phenocrysts has been described earlier (Boyd, 1970; Dence *et al.*, 1971; Hafner *et al.*, 1971). The crystal investigated here had a core $\sim 550 \mu$

in diameter in the XY plane surrounded by an epitaxial zone of pigeonite-titanaugite with microscopically exsolved augite lamellae observable in this zone. The absorption spectra of the pigeonite and titanaugite are shown in Figure 1. The possible Fe^{3+} tetrahedral spin-forbidden transitions are tabulated in Table II. Absorbance values in Figure 1 are only approximate above 4.0e (3100 Å) because of the intense absorption of the Fe^{3+} charge-transfer bands in the ultraviolet region. The anisotropy of the pigeonite was so small it was not studied in detail. Figure 2 gives the spectrum along the Y -axis, $\beta=b$ and in the XY plane near α . The lunar titanaugite has too intense an

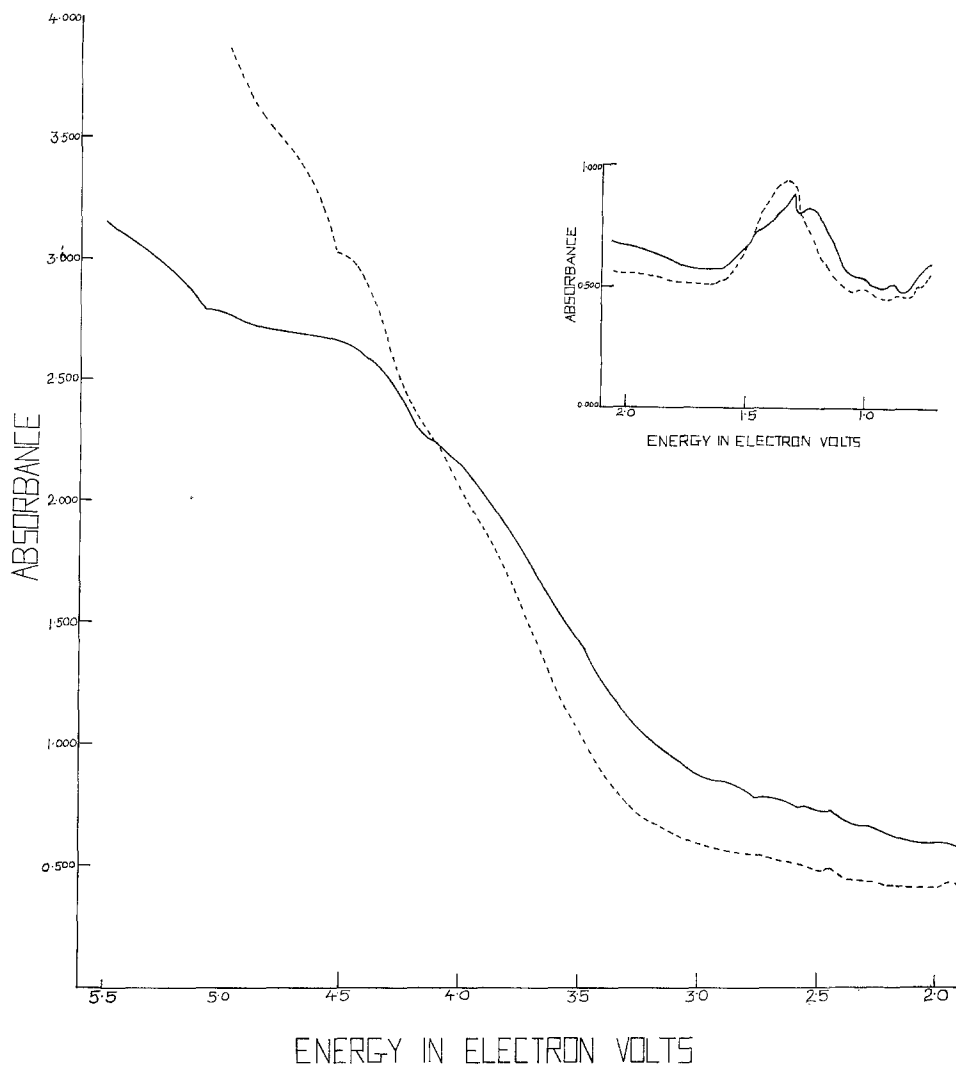


Fig. 1. Lunar Rock, 12021,65, pigeonite core surrounded by overgrowth of augite, orientation of 30μ thick section perpendicular to YZ plane. ---- spectrum of pigeonite core, $\sim 550 \mu$ diameter; — spectrum of augite overgrowth $\sim 250 \mu$ wide.

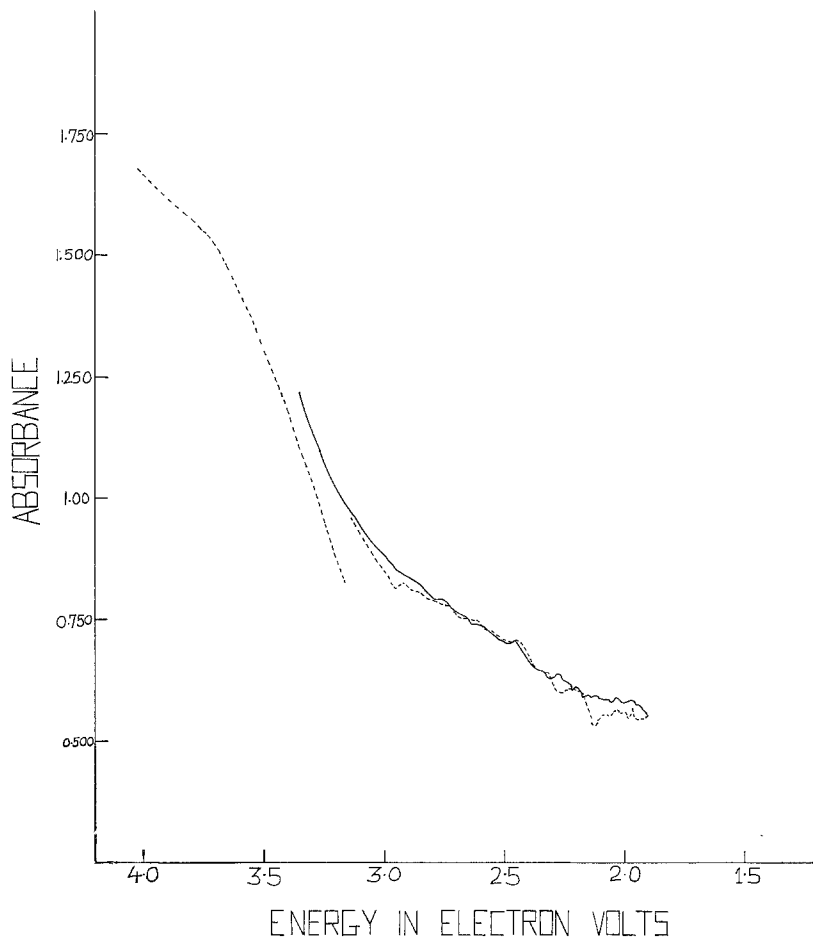


Fig. 2. Lunar Rock 12021,65. Polarized spectrum of augite zone.
 - - - - $b = \beta$; ——— in XY plane near α .

absorption to be measured above 5.5 eV ($\sim 2250 \text{ \AA}$) in Figure 1 and the Glan Polarizer limits the polarized spectrum to 4.0 eV in the β spectrum in Figure 2. Figure 3 shows the spectral data of augite from lunar rock 12018,50 after heating and Figure 4 that for Angra dos Reis meteoritic augite. Lunar rock 12018 was recovered at Oceanus Procellarum by the Apollo 12 mission. It contains smaller crystals of pyroxene than rock 12021 from the same mission and the transparent colored crystals are predominately titanite with some large crystals of olivine present. The rock is similar to a medium grained gabbro (Warner, 1970).

In Table II possible tetrahedral Fe^{3+} spin-forbidden transitions are listed for lunar augites in rocks 12018,50 and 12021,65. They are compared to data of Faye and Hogarth (1969) on phlogopite and orthoclase and to data run in this laboratory on augite from Haleakala, Maui, Hawaii and augite from the Angra dos Reis meteorite.

Chemical analyses for these augites with the exception of the one from rock 12018 are given in Table III.

The Hawaiian augite with 3.36 Fe_2O_3 has a band at 4470 Å (β) as its most prominent band in the visible region. The band at 4855 Å is much less intense and the one at 5300 Å barely discernable. The latter is more pronounced in the Angra dos Reis augite spectrum. The absorbance decrease in these bands compares favorably with those for the same transitions in phlogopite. The absorption bands in an unstrained tetrahedral position would be isotropic however the z -site in augite is somewhat distorted even though the distortion seems to decrease with substitution of Fe^{3+} (Hafner *et al.*, 1971).

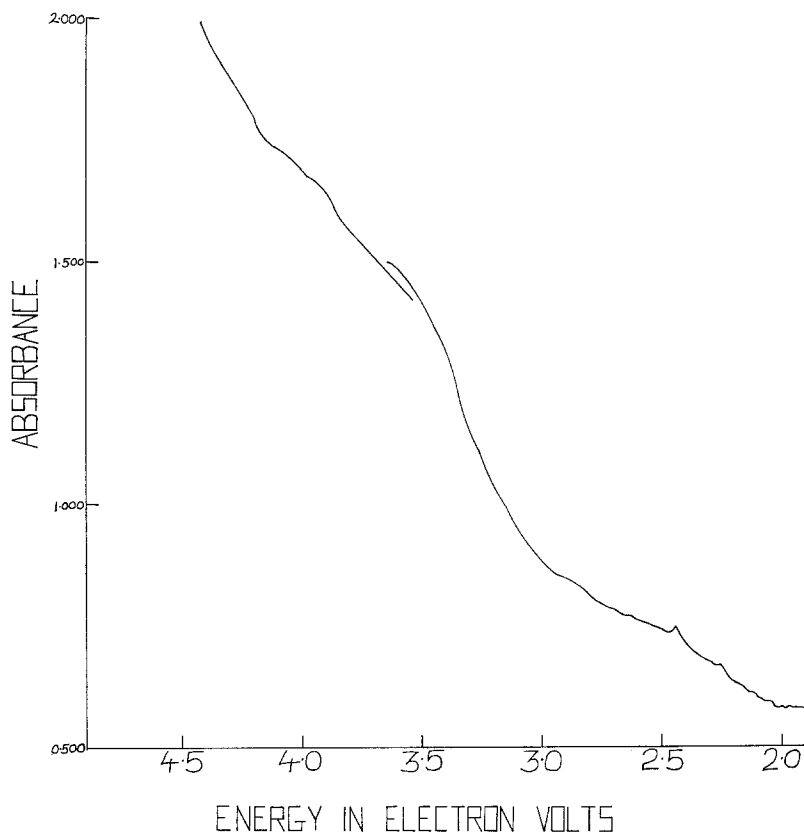


Fig. 3. Lunar Rock 12018,50 after heating at 200–225°C for 2 hr absorption spectrum of single crystal of augite $\sim 400 \mu$ diameter.

The bands are quite similar in the $\sim\alpha$ and β spectra although there are very slight wavelength shifts. The similarity of the $\sim\alpha$ and β spectra strengthen the probability that these are transitions of Fe^{3+} at a tetrahedral site. The presence of these bands in lunar augites strengthens the evidence for presence of Fe^{3+} in lunar minerals. Even though these assignments may turn out to be incorrect it does not preclude the

TABLE III
Chemical analyses of terrestrial, meteoritic, and lunar pyroxenes

Element as oxide	Haleakala, Maui Hawaii (Washington, 1922)	Angra dos Reis (Smales et al., 1970) ^a	Tatahouine (Reid and Cohen, 1967) ^a	12021 Lunar Pigeonite (Dence et al., 1970)	12021 Lunar augite (Dence et al., 1970)
SiO ₂	47.70	--	53.7	51.5	50.2
Al ₂ O ₃	6.82	21.5	0.45	2.05	3.32
Fe ₂ O ₃	3.36	--	--	--	--
FeO	4.43	8.4	13.89	16.9	13.1
MgO	13.34	--	28.2	21.9	15.3
CaO	21.35	~23.8	0.72	5.1	15.7
Na ₂ O	0.65	0.08	--	--	--
K ₂ O	0.03	0.012	--	--	--
TiO ₂	1.89	2.8	0.03	0.68	1.26
Cr ₂ O ₃	0.23	0.50	0.88	0.93	1.01
MnO	0.16	0.09	0.64	0.37	0.31
Totals	99.96		98.40	99.43	100.20

^a Whole meteorite analysis.

presence of Fe^{3+} in lunar augites as evidenced by the presence of charge transfer bands in the ultraviolet region.

There is a possibility that Fe^{2+} could occur at a z-site in the lunar augite as a result of radiation-reduction of Fe^{3+} located at this site. However the concentration would be low because of the small concentration of Fe^{3+} in the tetrahedral site.

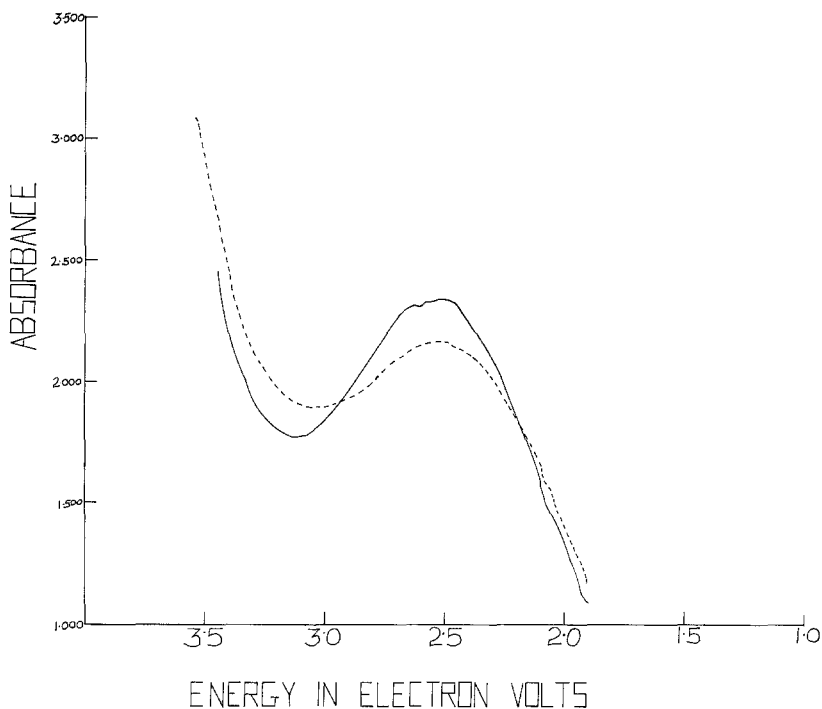


Fig. 4. Polarized absorption spectrum of single crystal of augite from Angra dos Reis achondrite, crystal cut perpendicular to YZ plane. ---- in XY plane near α ; — $b = \beta$. Crystal 50μ thick,

5. Fe^{3+} Charge-Transfer Bands in Lunar and Meteoritic Pyroxenes

Table IV lists probable oxygen ligand - Fe^{3+} metal charge transfer bands in Angra dos Reis augite, lunar augite, lunar pigeonite and Tatahouine achondritic hypersthene in the ultraviolet region. Reasons for possible site assignments of the bands at 2700-2850 Å, 2600-2700 Å, and 2200 Å were discussed in the introduction.

The earlier work on whole rock spectra did not furnish the spectral resolution of this later work on single crystals. For this reason additional bands were detected in augite in lunar rocks 12018 and 12021 at 2450-2500 Å. The Angra dos Reis meteorite as shown in Figure 5 has all these bands as well as an additional one at 2400 Å not found in the lunar augite. The pigeonite-augite zoned-crystal in rock 12021 had too great an absorbance to measure the respective regions down to 2200 Å. This is also the case with the Tatahouine meteoritic hypersthene which has a cutoff at 2750 Å.

TABLE IV
 Fe^{3+} charge transfer bands in the ultraviolet spectral region in single crystals

Possible site	M_1	$M_1(?)$	$M_2(?)$	M_2	z
Specimen	λ in A	λ in A	λ in A	λ in A	λ in A
Angra dos Reis augite	2750	2500	2400	2200	2600
Lunar:					
12018,50 augite	2850	2500	—	2200	2700
12021,65 augite	2700	2450	—	?	2700
12021,65 pigeonite	2750	—	?	?	2600
Tatahouine hypersthene	2800	?	?	?	?

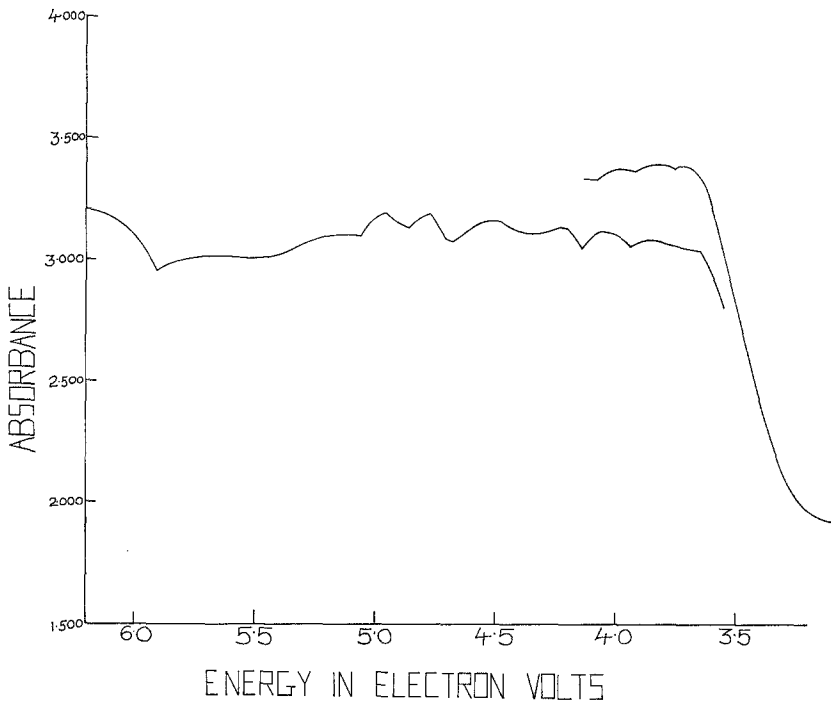


Fig. 5. Absorption spectrum of same crystal as in Figure 4 in the ultra-violet region showing charge transfer bands of Fe^{3+} .

6. Spin-Forbidden Fe^{2+} Bands in the Visible Region in Pyroxenes

Table V lists possible bands assignments to spin-forbidden bands of Fe^{2+} in octahedral sites. Earlier assignments of the bands of enstatite in this region has been published by White and Keester (1966). Burns and Huggins (1971) assigned bands at 402, 425, 505, 550 and 585 nm. in zoned-pyroxenes in lunar rocks 10045, 10047, and 10058 to spin-forbidden transitions of Fe^{2+} . This work is in agreement with their assignments

TABLE V
Spin-forbidden Fe^{2+} bands in visible region in pyroxenes

Transition ${}^5T_2(G) \rightarrow$	${}^4A_1{}^4E(G)$	${}^1T_1(G)$	${}^1A_1(G)$
Specimen	λ in Å	λ in Å	λ in Å
Maui, Hawaii augite	β 4090	β 4250	α 5040 n 5040
Angra dos Reis augite	α 4050 β 4100	α 4295	α 5000 n 5000
Lunar:			
12018,50 augite	—	—	5065
12021,65 augite	—	β 4250	α 5050 β 5050 n 5050
12021,65 pigeonite	—	—	5050
Tatahouine hypersthene	4050	4250	5060

n = normal unpolarized light.

Transition ${}^5T_2(G) \rightarrow$	${}^3T_1(G)$	${}^4T_2(G)$
Specimen	λ in Å	λ in Å
Maui, Hawaii augite	α 5400 β 5510 n 5450	β 5835 n 5805
Angra dos Reis augite	α 5585 β 5600 n 5550	α 5850 β 5890
Lunar:		
12018,50 augite	5500	5850
12021,65 augite	α 5650 β 5600 n 5500	α 5950 β 5950
12021,65 pigeonite	5500	—
Tatahouine hypersthene	—	—

n = normal unpolarized light.

of these bands to spin-forbidden transition of Fe^{2+} as shown by the data in Table V.

Mössbauer spectra of pyroxene in rock 12021 has been studied (Walter *et al.*, 1971) and indicates that the subcalcic augite has 0.34 of the M_1 site occupied by Fe^{2+} and 0.52 of the M_2 site while the pigeonite has 0.12 Fe^{2+} in the M_1 site and 0.46 in the M_2 site. The bands at 5050 and 5500 Å in the pigeonite are most likely due to Fe^{2+} in an M_2 site.

7. Charge Transfer Bands of Fe^{2+} and Ti^{3+}

Table VI lists bands at 6200 Å in augites that are probably due to $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+}$ charge transfer. A band in this region in corundum has been discussed by Faye (1971).

TABLE VI
Charge transfer bands of $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+}$ and $\text{Ti}^{3+} \rightarrow \text{Ti}^{4+}$

Specimen	$\text{Fe}^{2+} \rightarrow \text{Fe}^{3+}$	$\text{Ti}^{3+} \rightarrow \text{Ti}^{4+}$
Maui, Hawaii augite	6200 Å	α 4705 Å β 4750 Å
Angra dos Reis augite	α 6245 Å β 6200 Å	α 4805 Å β { 4750 Å 4705 Å
Lunar		
12018,50 augite	6200 Å	4700 Å
12021,65 augite	β 6200 Å	α 4750 Å β 4750 Å n 4800 Å
12021,65 pigeonite	6400 Å	4800 Å
Tatahouine hypersthene	6000 Å	—

n = normal unpolarized light.

The band in the region 4705–4800 Å is assigned to Ti^{3+} as a charge transfer band probably due to $\text{Ti}^{3+} \rightarrow \text{Ti}^{4+}$. It is probable that the Ti^{3+} is in the octahedral, M_1 , position.

The Ti^{3+} band is most intense in the Angra dos Reis meteorite because of its high radiation age (Ganapathy and Anders, 1971) and its high titanium content (Smales *et al.*, 1970). Tatahouine hypersthene is so low in titanium that this band is absent. It is also weak in pigeonite where the titanium present may be largely due to exsolved augite in the crystal.

8. Other Absorption Bands Related to Fe^{3+} or Fe^{2+} Spin-Forbidden Transitions

Table VII lists bands in the ultraviolet that are probably related to either Fe^{3+} or Fe^{2+} spin-forbidden transitions at an M site.

The terrestrial titanaugite had such intense absorption below 3700 Å that no data could be recorded.

Assignment of these bands will require further investigation. It is possible that a charge transfer component is present in several.

TABLE VII
Possible Fe^{3+} or Fe^{2+} spin-forbidden absorption bands in the ultraviolet spectral region

Specimen						
Maui, Hawaii augite	—	α 3750 Å	—	—	—	—
Angra dos Reis augite	3950 Å	3800	3350 Å	3250 Å	3100 Å	2950 Å
Lunar						
12018,50 augite	—	—	3350 Å	3250 Å	3150 Å	3000 Å
12021,65 augite	—	—	—	—	—	3000 Å
12021,65 pigeonite	—	—	—	—	—	—
Tatahouine hypersthene	—	—	—	—	—	2950 Å

9. Conclusions

The presence of Fe^{3+} in terrestrial titanite is expected and shown by analytical means. Comparison of lunar and meteoritic titanite to the terrestrial mineral indicates bands that may be attributed to tetrahedral Fe^{3+} ion in all specimens. Evidence for the presence of Fe^{3+} in lunar and meteoritic pyroxenes is strengthened by the charge transfer bands in the ultraviolet region. The major Fe^{3+} -related charge transfer bands in the ultraviolet are attributed to M_1 and M_2 sites in the augite structure. The decrease of these bands on mild heating is evidence that a portion of Fe^{3+} in octahedral sites is produced by radiation probably cosmic rays acting on Fe^{2+} .

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References

- Boyd, F. R.: 1971, Annual Report of the Director, Geophysical Laboratory, 1969-1970, Jan 1971, pp. 216-228.
- Burns, R. G. and Huggins, F. E.: 1971, Lunar Science Institute Conference on Lunar Geophysics, Oct. 18-21, 1971, Houston, Abstract.
- Cohen, A. J.: 1972, in S. K. Runcorn and H. C. Urey (eds.), 'The Moon', *IAU Symp.* **47**, in press.
- Cohen, A. J. and Hodge, E. S.: 1958, *J. Phys. Chem. Solids* **7**, 361-2.
- Cohen, A. J. and Hassan, F.: 1970, *Science* **167**, 176-177.
- Dence, M. R., Douglas, J. A. V., Plant, A. G., and Traill, R. J.: 1971, *Proceedings of the Second Lunar Science Conference* **1**, pp. 285-299, The MIT Press.
- Faye, G. N.: 1971, *Am. Mineral.* **56**, 344-348.
- Faye, G. H. and Hogarth, D. D.: 1969, *Can. Mineral.* **10**, 25-34.
- Ganapathy, R. and Anders, E.: 1969, *Geochim. Cosmochim. Acta* **33**, 775-789.
- Hafner, S. S. and Huckenholz, H. G.: 1971, *Nature Phys. Sci.* **233**, 9-10.
- Hafner, S. S., Virgo, D., and Warburton, D.: 1971, *Nature Phys. Sci.* **231**, 79-80.
- Hapke, B. W., Cohen, A. J., Cassidy, W. A., and Wells, E. N.: 1970, *Proceedings of the Apollo 11 Lunar Science Conference* **3**, pp. 2199-2212, Pergamon Press.
- Hapke, B. W., Cohen, A. J., Cassidy, W. A., and Wells, E. N.: 1970, *Science* **167**, 745-747.
- Reid, A. M. and Cohen, A. J.: 1967, *Geochim. Cosmochim. Acta* **31**, 661-672.
- Verhoogen, J.: 1962, *Am. J. Sci.* **260**, 211-220.
- Smales, A. A.: 1970, *Science* **167**, 509-512.
- Walter, L. S.: 1971, Second Apollo Conference, Houston, Jan. 1971, preprint.
- Warner, J.: 1970, NASA Technical Report R-353 Dec. 1970, p. 90.
- Washington, H. S.: 1922, *Am. J. Sci.* **3**, 117.
- White, W. B. and Keester, K. L.: 1966, *Am. Mineral* **51**, 774-791.