

Effects of compositional variation on absorption spectra of lunar olivines

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Abstract—Polarized absorption spectra of lunar olivines with a range of iron content (Fe_{50-87}) and chromium (0.07–0.61 wt.% Cr_2O_3) were measured on polished, oriented single crystals. No changes in spectra are observed with differing chromium content, but major increases in peak intensities and minor shifts in peak positions are observed with increasing fayalite content. All observed major features of olivine spectra are due to transitions in Fe^{2+} . Contributions, if present, from chromium and Fe^{3+} are masked in all reported lunar olivines thus far examined.

INTRODUCTION

IRON-BEARING SILICATES and oxides play a dominant role in determining the spectral properties of lunar rocks and soils. Correlations of absorption characteristics with compositional variations of lunar minerals are therefore important for correct interpretation of spectral reflectance data. Furthermore, data on absorption spectra are fundamental to the understanding of the valences of transition metal cations and, thus, the condition of formation of these minerals. In the present investigation polarized absorption spectra of lunar olivines are examined as a function of composition.

Complete polarized absorption (α , β , and γ) spectra have been reported for olivines from 10020 and 10022 (Burns *et al.*, 1972), 12040 (Bell and Mao, 1972a), 15555 (Bell and Mao, 1972b), and LUNA 20 (Bell and Mao, 1973), whereas partial spectra are available for 10020 (Haggerty *et al.*, 1970) and 15555 (Burns *et al.*, 1973). An important systematic investigation of terrestrial olivine spectra with a large compositional range was done by Burns (1970), but a similar effort for lunar specimens (Burns *et al.*, 1972) was restricted to a limited range of $Mg/(Mg + Fe)$. Burns and Vaughan (1975) reviewed the progress in understanding spectra of lunar olivines, and they noted the need for further studies to clarify the contributions of Cr^{2+} , Cr^{3+} , Fe^{2+} , and Fe^{3+} in lunar olivine spectra.

The principal objectives of this study are:

- (1) To correlate compositional variations of iron and chromium to absorption spectra variations.
- (2) To constrain models of the origin of olivine spectral features.
- (3) To compare lunar and terrestrial olivine absorption spectra.

EXPERIMENTAL

Single crystals of olivine, ranging from 200 to 500 μm in maximum dimension, were selected from lunar soils and rock fragments. Crystals were optically oriented, mounted in epoxy, and polished on both parallel sides to a thickness of 100–250 μm . Olivines were chemically analyzed at five points with an automated electron microprobe. Averaged analyses are presented in Table 1, with data for three olivines from previous studies. Polarized spectra of nine olivine crystals were measured using techniques described by Mao and Bell (1972a). After measurement of these spectra, crystals were removed from the epoxy, crystal thicknesses were measured, and the crystals were remounted and repolished at 90° to the original orientation. In this way complete α , β , and γ spectra were obtained.

Two of these olivine single crystals (from 12033 and 12070) were also examined by X-rays. It was confirmed that crystallographic axes a , b , and c correspond to optical axes γ , α , and β , respectively.

RESULTS

A typical polarized absorption spectrum of olivine (12070) is illustrated in Fig. 1. This spectrum is similar to that of previously recorded lunar and terrestrial olivines (e.g., Bell and Mao, 1972a, Fig. 2; Burns, 1970, Fig. 2). Broad bands between 900 and 1500 nm are interpreted by Burns (1970, 1974) and Runciman *et al.* (1974) as the result of transition to the highest energy state of Fe^{2+} in M(1) and M(2) based on systematic variation of band intensity with iron content. A prominent shoulder, usually ascribed to an ultraviolet charge-transfer band, appears below 600 nm. Superimposed on this shoulder are a number of weak, sharp peaks, most of which are assigned on the basis of their relative energies to spin-forbidden Fe^{2+} transitions (Burns, 1970). Less certain is the origin of the broad, weak band at approximately 625 nm (16,000 cm^{-1}). Burns (1970) and Runciman *et al.* (1973) attributed this band to a spin-forbidden Fe^{2+} transition in terrestrial olivines, due to its energy relative to other small peaks in the 400–600 nm region. Burns *et al.* (1973), however, ascribed the same band to a Cr^{3+} transition in lunar olivine, but a spin-forbidden Fe^{3+} transition (${}^6A_{1g} \rightarrow {}^4T_{1g}$) in terrestrial specimens, based on the similarity of the position of this peak to a Cr^{3+} band in a synthetic chromium olivine. Mao and Bell (1972b) examined the pressure-induced shift of this band in a terrestrial olivine, and suggested that the peak's behavior was consistent with Fe^{3+} – Fe^{2+} charge-transfer.

Additional confusion has resulted from reports of other small bands due to Cr^{2+} at 750 and 1040 nm (Haggerty *et al.*, 1970), and Fe^{3+} in the 400–500 nm region (Mao and Bell, 1971), as well as assignment by Burns *et al.* (1973) of a 450-nm peak to a Cr^{3+} transition in lunar olivines, but to an Fe^{3+} transition in terrestrial olivines.

To ascertain the chromium and iron contributions to lunar olivine absorption spectra, a group of crystals with similar iron but differing chromium content, and a group with similar chromium but differing iron content were selected. Figure 1 is the spectrum of the most chromium-rich olivine examined (0.6 wt.% Cr_2O_3). This spectrum shows no appreciable differences, either in peak shape or peak position, compared with other lunar olivines of significantly smaller chromium content. For example, consider the 625-nm peak illustrated in Fig. 2 for three Apollo 12 olivines with similar iron content (Fo_{65-67}) but large variation in

Table 1. Compositions of lunar olivines.

	10020.40 (1)	15555.205 (2)	LUNA 20-A9 (3)	12001-3	12001-4	12033-1	12033-3	12035-4	12070-2	12070-3	12070-4	70017-1
SiO ₂	37.5	36.22	39.93	37.33	36.98	36.27	36.93	35.28	38.30	37.41	37.20	36.38
TiO ₂	0.09	0.03	0.04	0.05	0.07	0.08	0.09	0.05	0.03	0.07	0.03	0.07
Al ₂ O ₃	0.05	0.05	0.02	0.00	0.02	0.05	0.01	0.02	0.06	0.09	0.09	0.05
Cr ₂ O ₃	0.21	0.33	0.40	0.31	0.07	0.21	0.13	0.07	0.46	0.61	0.38	0.30
FeO*	25.5	32.97	12.75	28.62	31.23	31.09	33.93	36.34	23.52	28.73	27.79	26.86
MnO	0.30	0.38	0.16	0.33	0.34	0.38	0.43	0.41	0.29	0.45	0.32	0.30
MgO	36.5	29.92	45.72	34.07	32.81	32.54	30.67	27.77	39.04	34.15	34.32	34.29
CaO	0.33	0.36	0.04	0.30	0.19	0.30	0.27	0.30	0.25	0.48	0.29	0.21
NiO	<0.01	†	0.03	<0.01	<0.01	0.06	0.05	<0.01	0.05	0.03	0.01	<0.01
Atomic proportions (based on 4 oxygens)												
Si	0.989	0.991	0.995	0.992	0.988	0.979	0.990	0.986	0.983	0.986	0.992	0.986
Ti	0.002	0.001	0.001	0.000	0.000	0.001	0.001	0.001	0.000	0.000	0.000	0.001
Cr	0.004	0.006	0.001	0.006	0.001	0.004	0.002	0.001	0.009	0.012	0.008	0.004
Fe	0.561	0.760	0.268	0.636	0.698	0.702	0.761	0.846	0.505	0.633	0.619	0.610
Mn	0.007	0.008	0.003	0.007	0.007	0.008	0.009	0.009	0.006	0.007	0.007	0.006
Mg	1.433	1.218	1.732	1.350	1.307	1.309	1.227	1.153	1.494	1.342	1.363	1.387
Ca	0.009	0.008	0.001	0.007	0.004	0.008	0.007	0.009	0.006	0.013	0.008	0.006

*Total Fe as FeO.

†No data reported.

(1) Haggerty *et al.* (1970).

(2) Bell and Mao (1972b).

(3) Bell and Mao (1973).

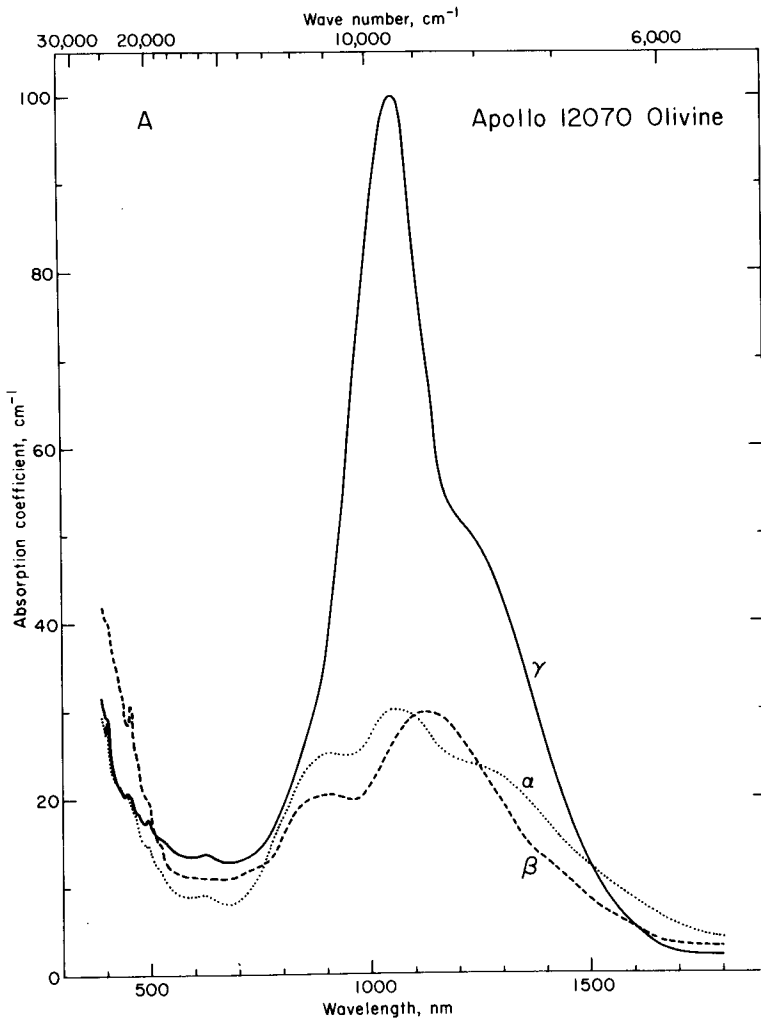


Fig. 1. Polarized absorption spectrum of Apollo 12070-3 olivine ($\text{Fo}_{67}\text{Fa}_{32}$, 0.61 wt.% Cr_2O_3): (a) from 400 to 1800 nm, (b) from 400 to 700 nm enlarged. This is the most chromium-rich lunar olivine for which spectral data are available, yet it shows no significant differences in peak positions or relative intensities compared with other lunar olivines.

chromium (0.07–0.61 wt.% Cr_2O_3). There are no appreciable differences in size or position of this peak with varying chromium content. Similar results were found for the 450-nm peak, ascribed to a Cr^{3+} transition by Burns *et al.* (1973). It is concluded, therefore, that there are no significant chromium contributions to lunar olivine absorption spectra over the compositional range represented in Table 1.

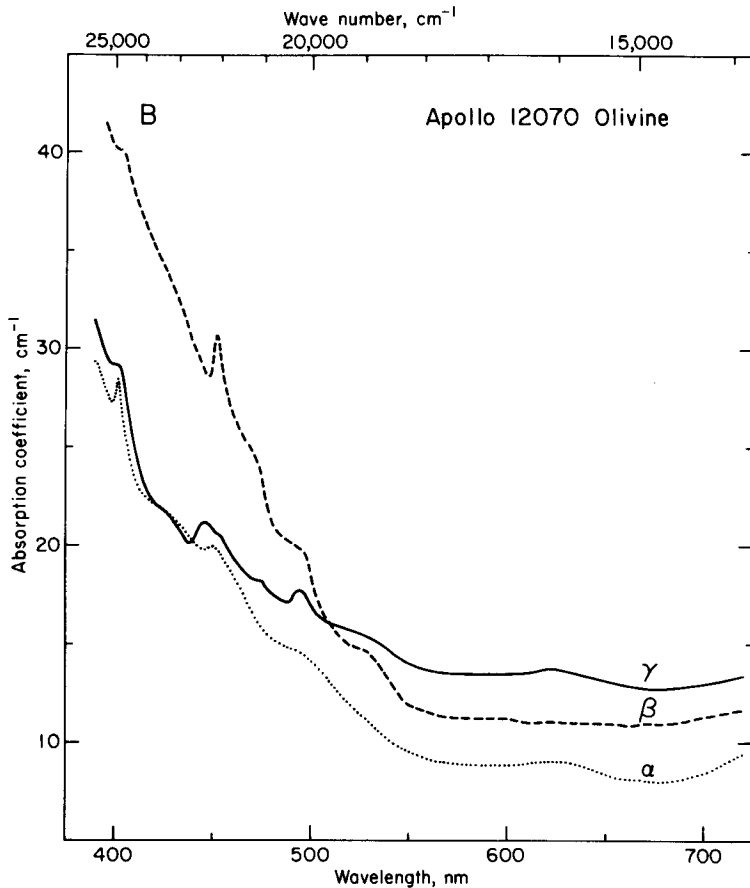


Fig. 1(b).

Changes in fayalite content have a dominant effect on olivine absorption intensity and a small effect on peak position. Figure 3 illustrates the variation of peak intensity and position for the 625-nm band with changing iron content (Fe_{50-87}) for four lunar olivines. Similar dramatic changes in intensity are observed in all other features in the olivine α , β , and γ spectra. A plot of maximum absorption coefficient for the 1060-nm γ -spectrum band versus iron content is shown in Fig. 4. The intensity of this band varies linearly with mol percentage of iron, indicating that absorption by iron behaves ideally between Fe_{87} and Fe_{50} for this band.

Positions of absorption maxima also change regularly with increasing fayalite content. Burns (1970) has clearly documented shifts to lower energies with increasing Fe_2SiO_4 for the major bands between 900 and 1500 nm. Lunar olivines display similar behavior, and positions of these absorption maxima lie near the curves suggested by Burns (1970, Fig. 3) and Burns *et al.* (1972). The position of

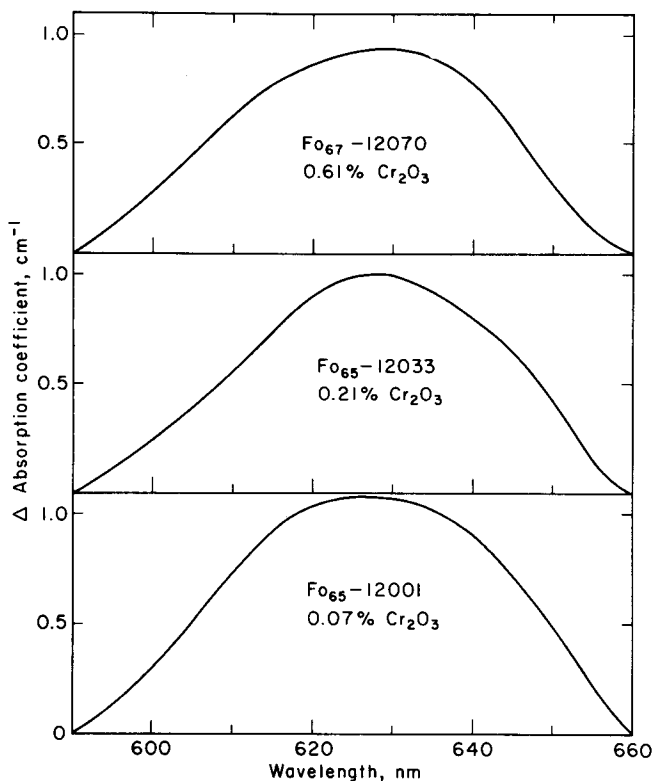


Fig. 2. Alpha spectrum peak at 625 nm for three different olivines with similar iron, but different chromium contents. The Δ absorption coefficient is obtained by subtracting the 590–660 nm background from the peak. Therefore, intensities at 590 and 660 nm are set to zero.

the 625-nm peak shifts to higher energy with increasing fayalite content (larger octahedral sites). Furthermore, the band shifts to lower energy at high pressure (smaller octahedral sites), as observed by Mao and Bell (1972b). This behavior is consistent with Burns' (1970) assignment of the peak to the ${}^3T_{1g}$ ferrous iron, spin-forbidden transition. Table 2 lists positions of absorption maxima for several lunar olivines of different fayalite content.

DISCUSSION

Comparison with terrestrial olivines

Lunar olivines are remarkably similar in absorption properties to their terrestrial counterparts. Excluding spectra of those terrestrial olivines with high Mn, Ca, or Ni, and low Fe, the peak positions and relative absorption intensities

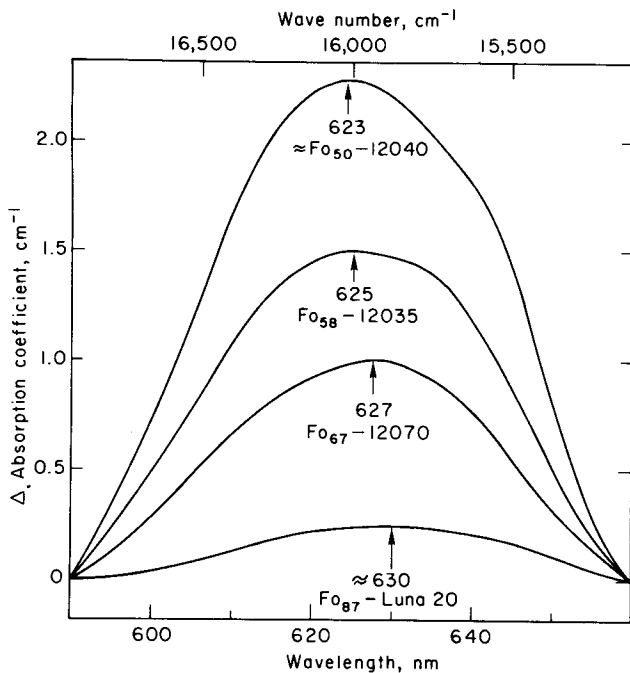


Fig. 3. Alpha spectrum peak at 625 nm versus Δ absorption coefficient. The Δ absorption coefficient is obtained by subtracting the 590–660 nm background from the peak. Therefore, intensities at 590 and 660 nm are set to zero.

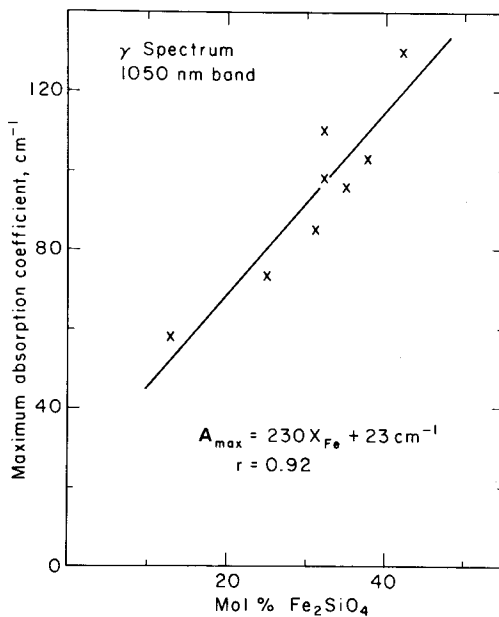


Fig. 4. Intensity of the ≈ 1060 -nm γ -spectrum band versus mol percentage of fayalite in lunar olivines. Absorption intensity increases with greater iron content.

Table 2. Absorption spectra peak positions versus forsterite content for lunar olivines.

Specimen	Fo _x	α						β						γ		
		400-410	440-450	620-630	1000-1100	450-460	850-950	1050-1200	440-450	490-500	620-630	1050-1060	450	*	*	
LUNA 20 (1)	Fo ₈₇	*	*	630	1050	*	*	1080	450	*	*	450	*	*	1050	
12070-2	Fo ₇₅	402	≈ 450	630	1050	453	915	1100	≈ 445	*	*	≈ 445	*	*	1055	
12070-3	Fo ₆₇	402	450	627	1055	452	910	1130	446	495	623	446	495	623	1058	
12001-3		401	454	627	1070	453	910	1135	445	493	626	445	493	626	1060	
12033-1	Fo ₆₅	401	455	625	1078	453	900	1155	446	*	620	446	*	620	1057	
15555,205 (2)	Fo ₆₁	401	457	625	1075	450	890	1150	445	≈ 495	623	445	≈ 495	623	1063	
12035-4	Fo ₅₈	400	454	623	1075	451	888	1150	448	495	622	448	495	622	1060	
12040,18 (3)	≈ Fo ₅₀	†														

*Peak not clearly resolved.

†Not reported.

(1) Data of Bell and Mao (1973).

(2) Data of Bell and Mao (1972b).

(3) Data of Bell and Mao (1972a).

are similar for all specimens examined. The reasons for this similarity are evident from an examination of the olivine crystal structure. Any substitution of ferric iron for ferrous iron requires the introduction of vacancies if charge balance is to be maintained. Specifically,



where Fe^{2+} , Fe^{3+} , and vacancies are disordered between M(1) and M(2) octahedral sites. The presence of vacancies may cause severe local charge imbalance. Furthermore, Fe^{3+} is significantly smaller than Fe^{2+} in octahedral coordination and will cause local distortions of the olivine structure. Duba *et al.* (1973) have established that at high oxygen fugacities, olivine will exsolve magnetite (and, presumably, SiO_2) rather than accept significant ferric iron in M(1) and M(2). Therefore, because the orthosilicate structure can accommodate only minor amounts of ferric iron, ferrous iron transitions dominate the spectra. Contributions from chromium, Fe^{3+} , and other transition metal cations are masked by the strong Fe^{2+} effects. It is not surprising, therefore, that olivines from environments with as different oxygen fugacities as those of the earth and moon should display indistinguishable optical properties.

CONCLUSIONS

As indicated above, the interpretation of polarized absorption spectra of lunar minerals has been greatly hampered by the lack of systematic data. The present study on olivine, as well as work in progress on lunar pyroxenes, places constraints on band assignments by determining systematic variations of absorption spectra with composition. Band assignments may be made with less ambiguity following these procedures.

It is concluded that the polarized absorption band near 625 nm in lunar and terrestrial olivines does not correlate with chromium or ferric iron content as had been previously thought. Assignments of the band to spin-allowed transitions in Cr^{3+} and to spin-forbidden and charge-transfer transitions in Fe^{3+} are not documented and are probably incorrect. The intensity of the 625-nm band correlates, however, with the amount of Fe^{2+} (and total Fe) in a given olivine, whether of lunar or of terrestrial origin. The band is commonly observed in spectra of iron-bearing olivine, and although no definite electronic transition is determined as its cause, the absorption is possibly related to a spin-forbidden type of crystal-field transition in Fe^{2+} .

It is significant that band intensity can be used as a measure of the iron content (fayalite component) in a spectral region (visible) best suited for interpretation of spectra obtained by earth-based telescope (Adams, 1974; Gaffey, 1976).

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