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THERMODYNAMICS OF FE-MG OLIVINES AT MANTLE PRESSURES: MID- AND FAR-
INFRARED SPECTROSCOPY AT HIGH PRESSURE

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FOR DEPOSIT: APPENDIX FIGURES AND TABLES

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Figure Captions for the Appendix

Fig. A1. Sketch of the all-reflecting beam condenser for use with the megabar diamond anvil cell in the FTIR spectrometer. The ellipsoidal mirror (6X magnification) focuses light onto the interface between the two diamond anvils (the sample chamber). The standard diamond cell occludes about 10-15% of the light coming in. A beveled entrance to the cylinder (dotted area) would increase the intensity. Because of the shadowing, the overall increase of throughput is four to five times that without the beam condenser in the mid-IR. The light cone (black area) consists of two pieces: a plug for the rocker with a polished cylindrical hole, and a cone with 7° interior angle. The cone is crucial to the functioning of the beam condenser, in that it funnels the light out of the piston (stippled area) such that the wide end of the cone acts as a focal point. All of the mirrors (M2-M5) and the light cone are polished aluminum.

Fig. A2. Far-IR absorption spectra of natural magnesian olivine (Fo#87). Spectra were taken at pressures of a single-crystal in the DAC are labeled in kbar. The 0 kbar spectra was taken of powder in a KBr pellet. Due to sample thickness, the spectra at pressure are essentially opaque at $\nu > 300 \text{ cm}^{-1}$ producing much noise in this area. Water vapor produces the weak bands below 125 cm^{-1} . Spectra are offset for clarity. The absorbance for all at $\sim 100 \text{ cm}^{-1}$ is approximately zero. Spectra were baseline corrected and water peaks were subtracted.

Fig. A3. Far-IR spectra of fayalite powder taken during decompression. Labels are pressures in kbar. The peak at 200 cm^{-1} is a B_{1u} component that was not detected in the single-crystal experiments. The large breadth of the highest energy peak at 290 cm^{-1} at 1 atm and its proximity to the cutoff limit of the bolometer made it difficult to determine

accurately the position of this peak as a function of pressure by locating the maximum intensity. Instead, the point where the slope changes (indicated by a star).

Fig. A 4. Peak positions of natural olivine as a function of pressure.

Symbols are as in Table 1 except that all runs were non-hydrostatic. The light dotted lines are the trends of Fo=100 with pressure. Below 100 kb, frequency appears to linearly depend on pressure. Filled symbols are data taken during decompression.

Fig. A 5. Peak positions of natural olivine as a function of volume. Symbols as in Table 1. All frequencies appear to follow linear trends with volume up to the maximum pressures attained (200 kbar). Filled symbols indicate data collected during decompression.

Fig. 6. Dependence of fayalite peak widths on volume. Bottom, far-IR data. Filled symbols are from powder; others are single crystal data. Top, widths from mid-IR powder spectra of Xu et al. (1983). True widths increase gradually with pressure for all peaks except 3 (cross). The separation of doublet 3 creates a false width that increases drastically, whereas the true width (filled crosses) increases slowly.

Fig. 7. Peak intensity as a function of volume during decompression of olivine. Top, synthetic forsterite. Open symbols, hydrostatic runs. Filled symbols, non-hydrostatic runs. Middle, natural olivine. Bottom, fayalite. Mid-IR peaks are indicated by slashed symbols (Table). Intensities are nearly independent of volume or pressure for peak 1 (circle), 5 (cross), and 9 (open). Intensity increases with pressure for peak 2a (triangle). For all other peaks (mid- and far-IR energy regions) intensity decreases as pressure increases (or volume decreases).

Fig. A.8. Log-log plot of band positions of natural olivine vs. volume.
Symbols are as in Table 1. A linear trend of $\log \gamma$ with \log volume occurs
for all bands observed over all pressures measured.

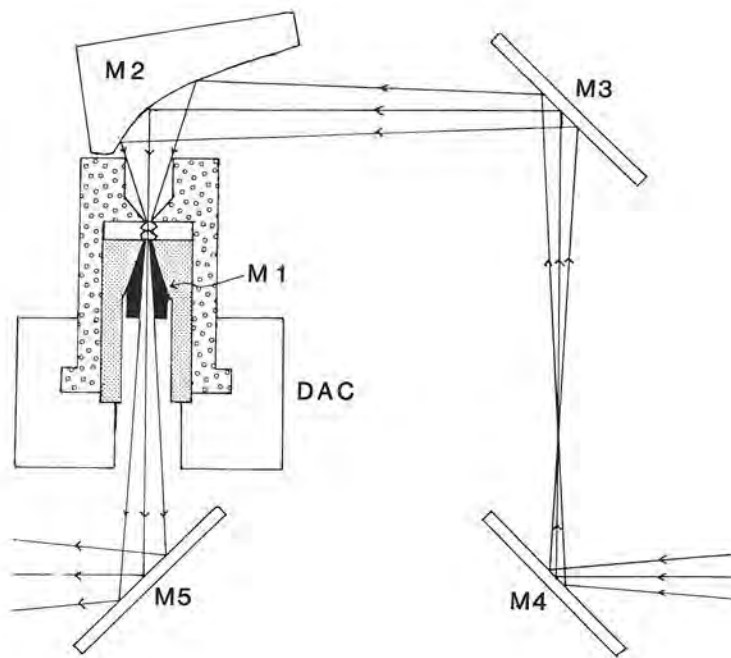


Fig. A1

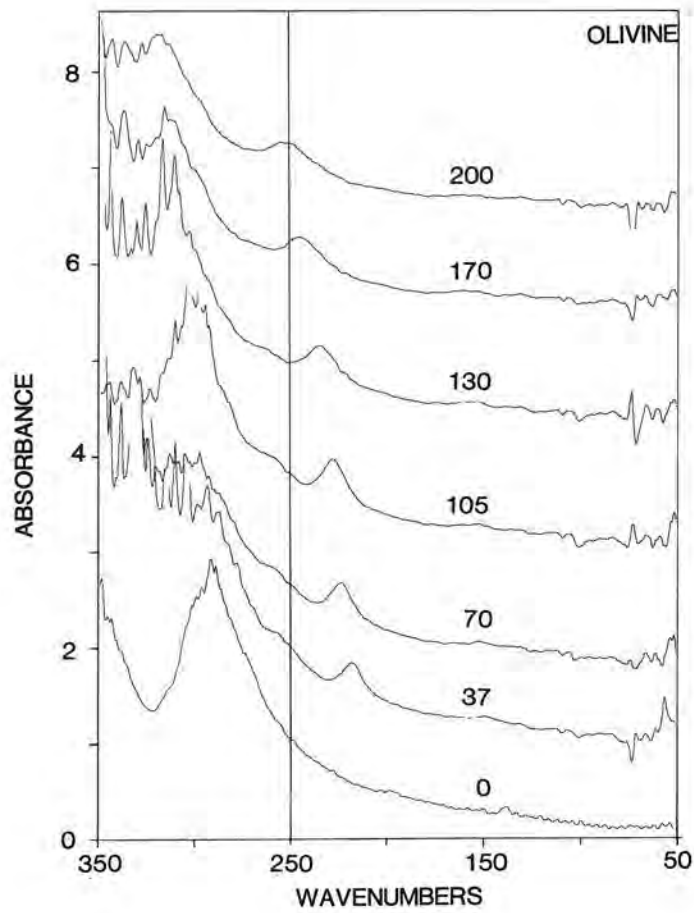


Fig A2

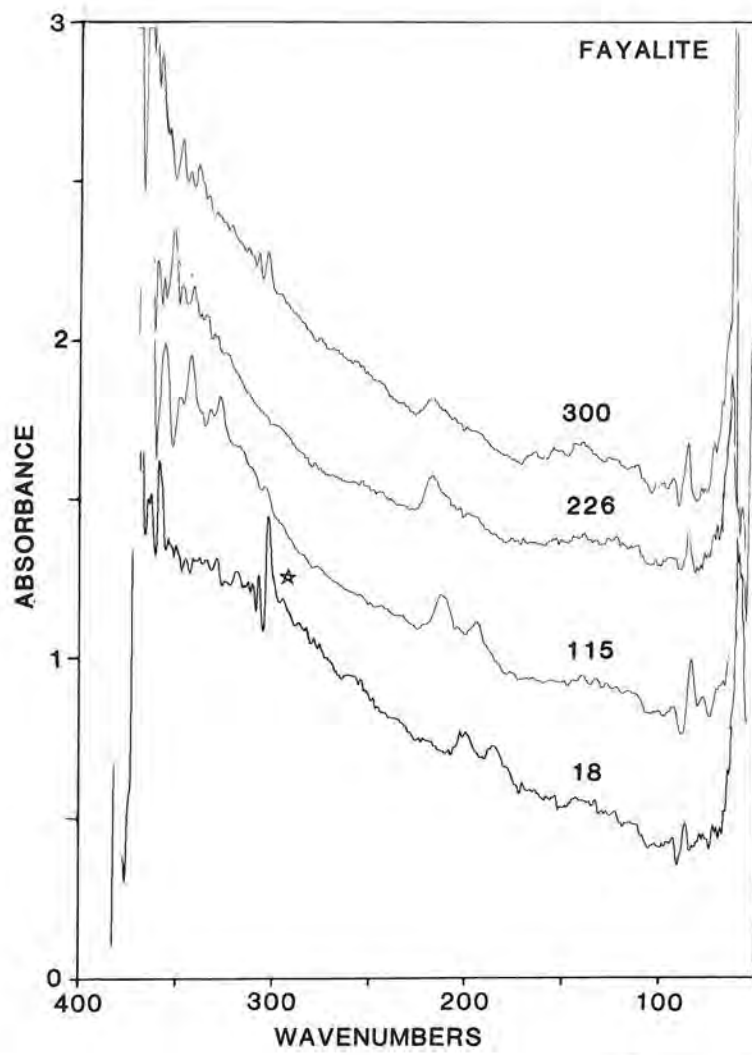


Fig. A3

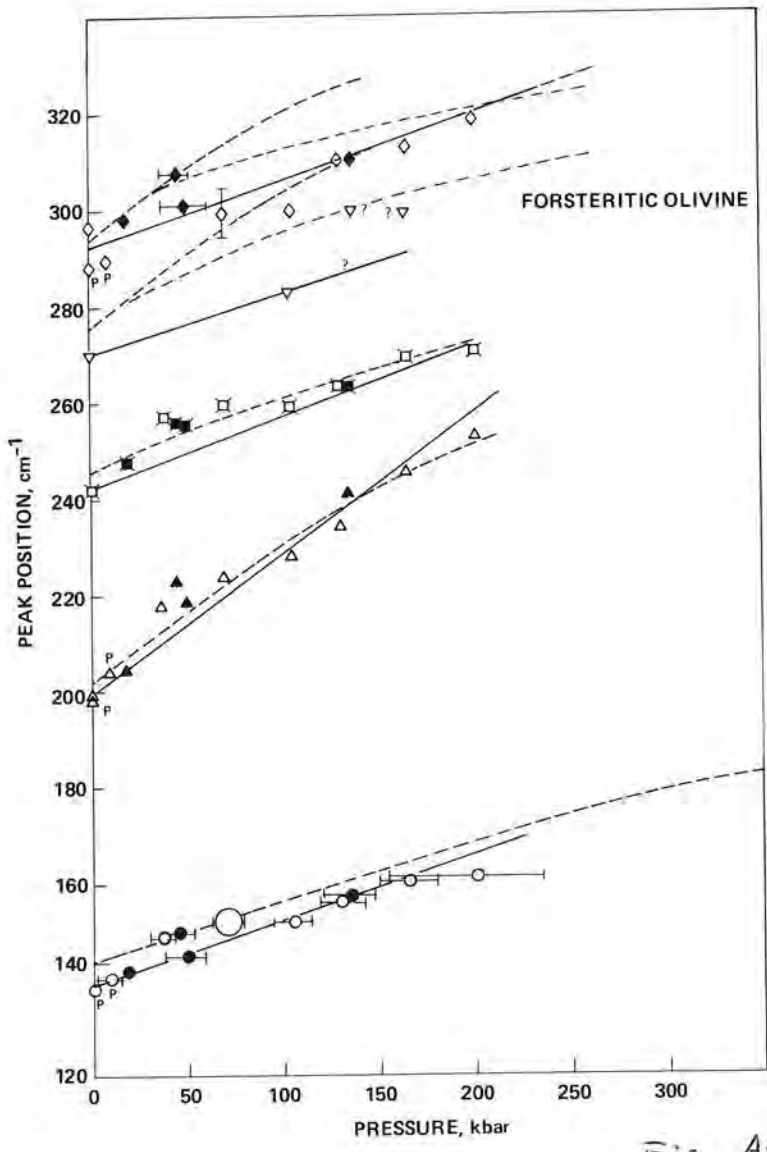


Fig. A4

Fig. A5

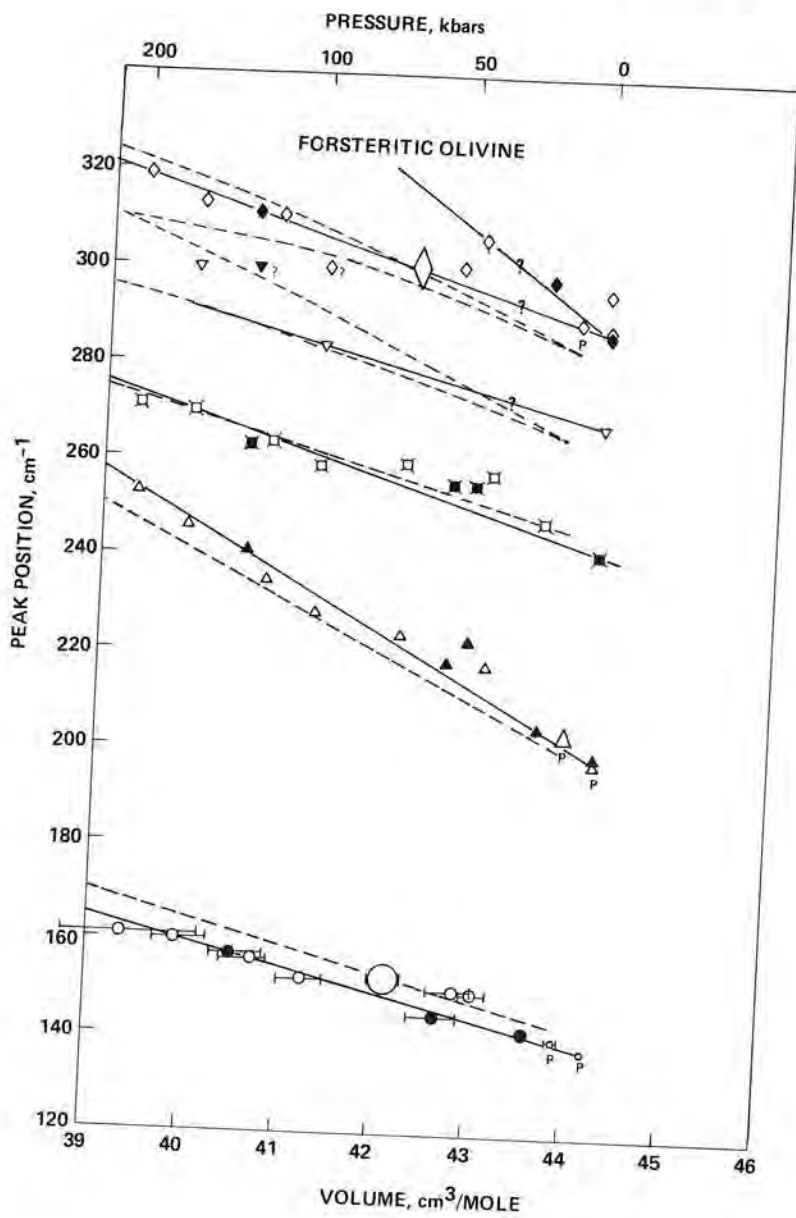


Fig. A6

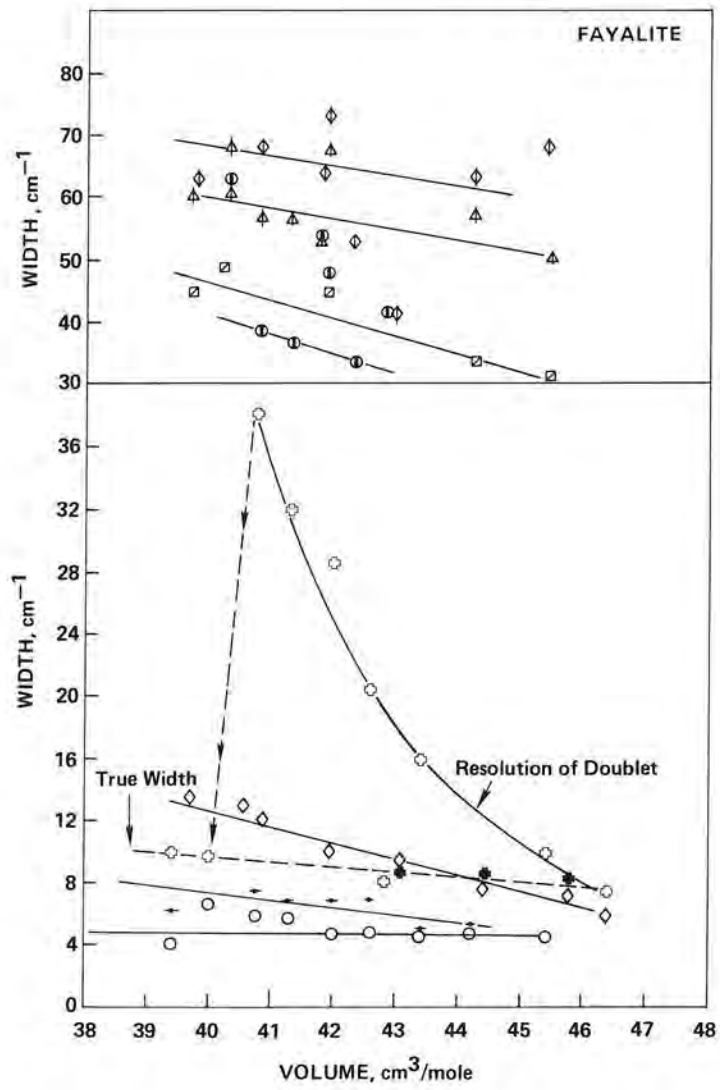
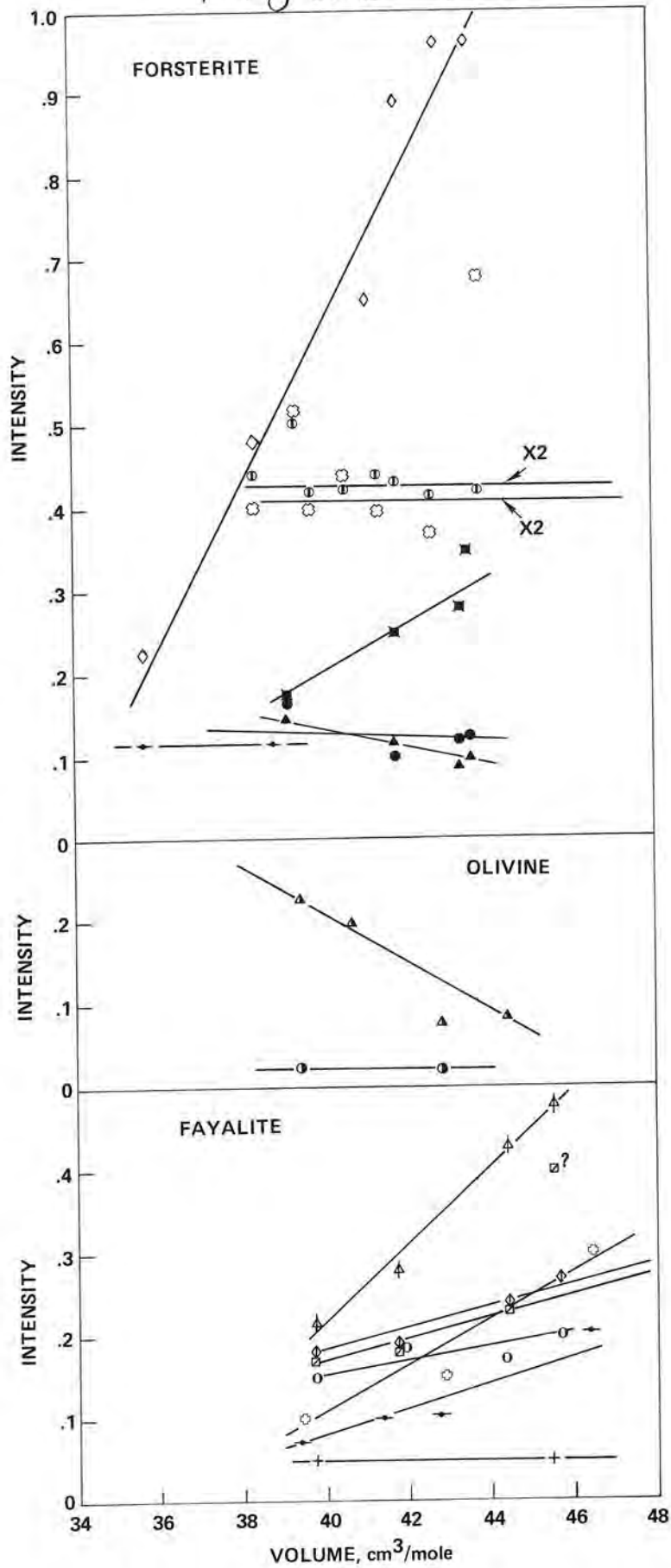


Figure A7



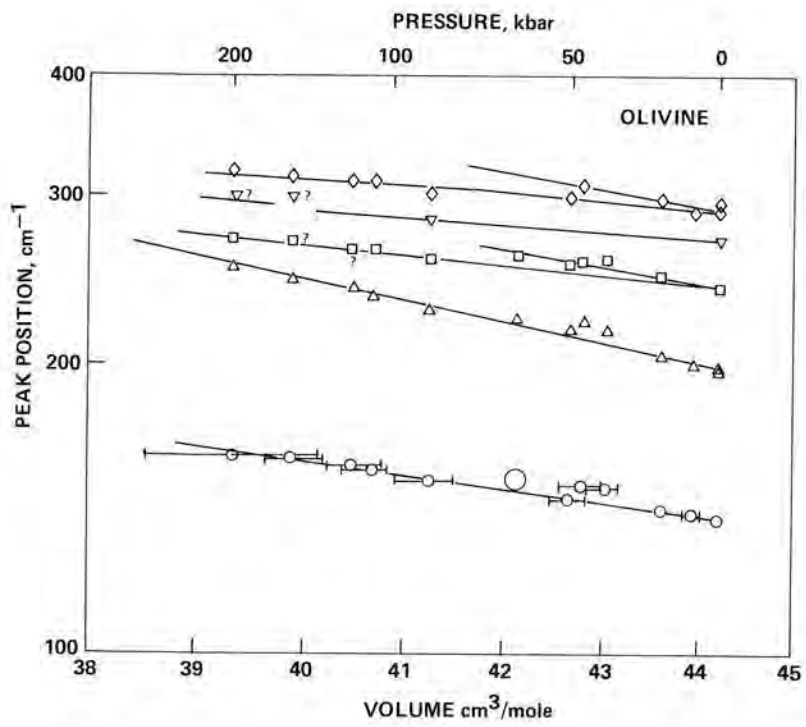


Fig
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Table A1. Chemical analysis of Natural Olivines

Mineral	Forsterite-87*		Fayalite@	
Location	Balsam Gap, N. Carolina		Inyo Co., California	
Sample No.	Geophysical Laboratory P-140		National Museum Natural History #115212	
	wt%	formula&	wt%	formula&
SiO ₂	40.85	0.954	29.28	0.990
TiO ₂				
Al ₂ O ₃	0.13	0.036	trace	
FeO	7.17	0.275	65.28	1.843
MnO	0.074	0.001	4.39	0.126
MgO	51.63	1.798	1.05	0.005
CaO			trace	
Na ₂ O	0.02		ND	
K ₂ O	10.004			
NiO	0.30	0.006	ND	
Total	100.17	3.07	100.00	2.96
mole% Fo	87.0		0.2	
Fa	13.0		93.4	
Te	~0.0		6.4	
sc	2.4 ppm			
co	140 ppm			
cr	75 ppm			

* Wet chemical analysis provided by F.R. Boyd (Geophysical Laboratory)

@ Microprobe analysis by M. Schaefer (Naval Research Laboratory
& Formula based on four oxygens; ND, not determined.

Table A2. Pressure Dependence of Synthetic Forsterite Far-IR Peak Parameters (non-hydrostatic)

Pressure Kbar	0.001*	64±8	95±10	125 20	195±25	70±10(D)	20±5(I2)	8±1(I3)
Vol., cm ³ /mole	43.80	41.86	41.11	40.43	39.07	41.72	43.14	43.52
λ(1)	144	152	157.39	161.55	166.91	155.2	146.5	144.72
width		8.7	9.05	8.66	9.70	-10.5	7.50	7.50
intensity		0.25	0.26	0.24	1.64	0.10	0.12	0.13
area		2.20	2.36	2.04	1.60	1.19	0.90	1.01
λ(2)	201	{ 222.80 228.04	231.6	240.7	{ 243.3 251.4	228	206 211	208
width		-14	12.6	15.0	16	-10	-11	-12
intensity		0.23	0.22	0.17	0.15	0.12	-0.09	-0.1
area		3.4	2.7	2.6	2.4	-1.2	-1.0	-1.2
λ(2b)	ca 246?	253±259	260.9	265.8	269.7	258.4	~250	247.4
width		-15.0	11.0	9.49	11.8	10.1	9.9	9.2
intensity		0.63	30.37	0.29	0.17	0.25	0.28	0.35
area		9.5	4.05	2.76	2.00	2.50	2.73	3.20

Note: (D) = decreasing; (I2) = second increase in pressure

*Powder spectrum not taken in a DAC

Table A.3. Pressure Dependence of magnesian-olivine (FO-87) single-xtal Far-IR Peak Parameters

Pressures kb	0.001*	8±1\$	37±5	70±7	105±10	130±10	170±15	200±35	135±10@	45±7@	0±1@
Vol., cm ³ /mole	44.20	43.93	43.02	42.11	41.26	40.71	39.91	39.35	40.60	42.78	44.2
λ(1)	138	140.5	149.54	152.65	152.1	156.1	160.1	160.9	~157	150	
w 1/2		5.7	6.8	7	~7	~10	~15	~13		~8.5	
I			0.034	0.033	0.035	0.03	0.03	0.025		0.023	
II			0.23	0.21	~0.25	~0.3	~0.5	~0.3		~0.2	
λ(2a)	198	~204?	218.22	223.98	228.4	235.32	246.0	~253	241.7	223	199.5
w 1/2			9.0	9.8	11.4	14.8	14.7	18	16	13	7.4
I			0.27	0.3	0.36	0.3	0.22	0.23	0.2	0.08	0.09
II			2.43	2.96	4.10	4.4	3.2	4.1	8	1.04	0.66
λ(2b)			257.7	259.7	258.4	263.6	270?	271?	263?	~256	~242
w 1/2			6.6	6.8	4.5						
I			0.12	0.1	0.08						
II			0.8	0.7	0.4						
λ(4)		290			300	311	313	319.0	311.0	307.6	296.7
w 1/2					18.8		18	20	~14	~18	~30
I					1.17		0.8	0.62	0.58	0.59	0.55
II					22		14.4	12.4	~8.1	~11	~16

*Powder outside DAC

\$Powder data in DAC

@Decreasing pressure

#Second increase of pressure

Table A4. Pressure dependence of Fayalite Peak Parameters, for powdered sample

Pressure, kbar	0.001*	18±0.1	63±1	116±2	170±2	226±2	245±3	300±5	150±3	36±0.3
Vol, cm ³ /mole	46.39	45.763	44.395	43.073	41.937	40.860	40.540	39.687	42.300	45.184
λ(4c)	184	185.2	191.1	194.1	~196	196.6	~197	~196	193.2	187.6?
width	7.7	~8.4	8.5	<8.9						
intensity		0.093	0.107	0.109						
area		0.78	0.91	<.97						
λ(4b)	184					~208	~208			
λ(5)	197.6	200.2	207.0	212.1	215.8	217.1	217.6	217.1	210.8	202.3
width	<7.7	7.2	7.6	~9.4	10	12	13	13.6		~7
intensity		0.087	0.090	0.129	0.144	0.143	0.121	0.052		-0.05
area		0.63	0.68	1.2	1.4	1.7	1.6	0.71		-0.35
λ(8)	252	257								
λ(9)	290	296	318±6	320±7	326	339	348	355±5		~300

Table A5. Mid-IR band positions of synthetic forsterite (T.J. Shankland sample).

Pressure, kbar	134±2	186±4	240±5	181±7	157±7	123±6	86±5	69±4	35±3	1±1
Volume, cm ³ /mole	40.255	39.255	38.305	39.318	39.769	40.463	41.321	41.753	42.673	43.766
v(8??)			416.4							
v(9+10a)	447	458±2	465.5	457.0	447.8	444	440±5	440±1	433	425.8
width	86	104	100	95	100	100	~75		94	~50
intensity	0.54	0.31	0.20	0.26	0.20	0.22	0.20		0.185	0.34
area	46.4	32.2	20	25	20	22	15		17.4	16.8
v(10+11+12)	499	512?	519.7	512.4	510.3	{512 489	488?	495		{465.3 501.2
v(14+15)	596	604	617	600	589	583	576	567	563	546
v(16)	624	636	652	635	630	629	623	619	608	610.2
width	~98	96	100	96	100	100	100	100	100	~100
intensity	0.51	0.30	0.22	0.26	0.21	0.21	0.22	0.218	0.207	0.21
area	50	29	22	25	21	21	22	21.5	20.7	21
v(16b)	689	699	715.2	700	694	690 (725?)	704?	690? (723?)	{665? 686?	~700?
v(17)							852	856	849.6	835.6
v(18)	910.1	914	927.6	910.5	910	903.5	898	892	878	877.8
v(20)							1020?	1007?		988

Table A 7. Mid-IR forsterite data from Xu et al. (1983)*

Pressure, kbar	0.001	3±1	19.4±1	49±5	92±1	139±5	177±6	198±8
Volume, cm ³ /mole	43.79	43.70	43.159	42.29	41.172	40.14	39.396	39.00
λ(15)	542							
λ(16a)	606-609			628	645	653.1	665.5	660.3
width	~50					50	48	42
intensity						0.154	0.115	0.14
area						7.7	5.5	5.9
λ(17)	837-839					~880		906
λ(18)	884-885	889.6	892.7	906.0	919.1	923.3	928.9	937.0
width			40			38	40	38
intensity						0.192	0.105	0.14
area						7.1	4.2	5.2
λ(19)	925 sh				939.5	957	959	962
λ(19,LO)	953-957							989
λ(20)	988	991.8	997.4	1012.1	1037.1	1054.5	1078.1	1086.7
width			38			49	66	66
intensity						0.13	0.09	0.11
area						6.3	5.9	7.5

*Widths could not be accurately measured for most spectra because interference fringes were present.