

WADSLYITE, NATURAL β -(Mg, Fe)₂SiO₄ FROM THE PEACE RIVER METEORITE

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ABSTRACT

Wadsleyite, a new mineral species, occurs as a fine-grained material in fragments within a vein in the Peace River meteorite (Alberta); it was formed by a series of polymorphic phase transformations, from olivine and ringwoodite, during an extraterrestrial shock event. Wadsleyite has the structure of the β -phase polymorph of (Mg,Fe)₂SiO₄ and an ideal composition of (Mg_{1.5}Fe_{0.5})SiO₄. Single crystals of wadsleyite rarely exceed 5 μ m in diameter; polycrystalline aggregates are transparent with a pale fawn coloration and a bulk index of refraction of 1.76. The strongest six reflections in the X-ray powder-diffraction pattern [d in Å (I) ($h k l$)] are: 2.89(m) (040), 2.69(m) (013), 2.45(s) (141), 2.04(s) (240), 1.57(m) (303), 1.44(s) (244). Wadsleyite is orthorhombic with a 5.70(2), b 11.51(7), c 8.24(4) Å, V 541(3) Å³, Z = 8 and, on the basis of the ideal formula, has a calculated density of 3.84 g cm⁻³. All observed X-ray and electron-diffraction data are compatible with space group *Imma*. The new species is named after the late Dr. A. D. Wadsley.

Keywords: wadsleyite, new mineral species, β -(Mg, Fe)₂SiO₄, polymorph, mantle mineral, shock event, meteorite, Peace River (Alberta).

SOMMAIRE

La wadsleyite, espèce nouvelle, se présente en matériau finement grenu dans des fragments à l'intérieur d'un filon dans la météorite de Peace River (Alberta). Elle s'est formée par transformations polymorphiques, à partir d'olivine et de ringwoodite lors d'un événement-choc extraterrestre. La structure est du type β -(Mg,Fe)₂SiO₄, avec (Mg_{1.5}Fe_{0.5})SiO₄ comme composition idéale. Les monocristaux excèdent rarement 5 μ m de diamètre; les agrégats polycristallins sont transparents et possèdent une faible coloration fauve et un indice de réfraction moyen de 1.76. Les raies les plus intenses du cliché de poudre [d en Å(I)($h k l$)] sont: 2.89(m) (040), 2.69(m) (013), 2.45(s) (141), 2.04(s) (240), 1.57(m) (303), 1.44(s) (244). La wadsleyite est orthorhombique avec a 5.70(2), b 11.51(7), c 8.24(4) Å, V 541(3) Å³ pour Z = 8; sa densité calculée à partir de la formule idéale est de 3.84. Toutes les données de diffraction X et de diffrac-

tion électronique sont compatibles avec le groupe spatial *Imma*. La nouvelle espèce honore feu le Dr. A.D. Wadsley.

(Traduit par la Rédaction)

Mots clés: wadsleyite, nouvelle espèce, β -(Mg,Fe)₂SiO₄, polymorphe, minéral du manteau, météorite, événement de choc, Peace River (Alberta).

INTRODUCTION

Wadsleyite, a new mineral species found in the Peace River meteorite (Alberta), is the naturally occurring β -phase polymorph of (Mg, Fe)₂SiO₄. The occurrence of the β -phase as an intermediate in the high-pressure transformation of magnesium-rich olivine to its spinel-structure polymorph was first reported by Ringwood & Major (1966). The β -phase was subsequently confirmed to have a stability field by Akimoto & Sato (1968), Akimoto (1970) and others, who performed further studies on the system (Mg, Fe)₂SiO₄ and also synthesized isostructural analogues with compositions Co₂SiO₄, Mn₂GeO₄, Ni₃Al₂SiO₈ and Zn₂SiO₄.

Phase equilibria in the solid-solution series Mg₂SiO₄-Fe₂SiO₄ have been widely studied because the polymorphic phase transformations in this series are believed to determine directly the structure of the earth's mantle. In particular, the β -phase polymorph of (Mg,Fe)₂SiO₄ is expected to comprise a significant proportion of the transition zone of the mantle. Obviously, since no mantle-derived β -phase is available, the study of this compound has previously been restricted to synthetic material. The discovery of wadsleyite in the Peace River meteorite is particularly important, therefore, because of the further insight into the behavior of this mantle-forming material that can be obtained by studying the naturally produced β -phase.

It was originally proposed by Ringwood & Major (1970, p. 107) that if β -(Mg,Fe)₂SiO₄ were ever to be found in nature, it should be named *wadsleyite* in honor of the late Dr. A. D. Wadsley, "whose outstanding crystallographic

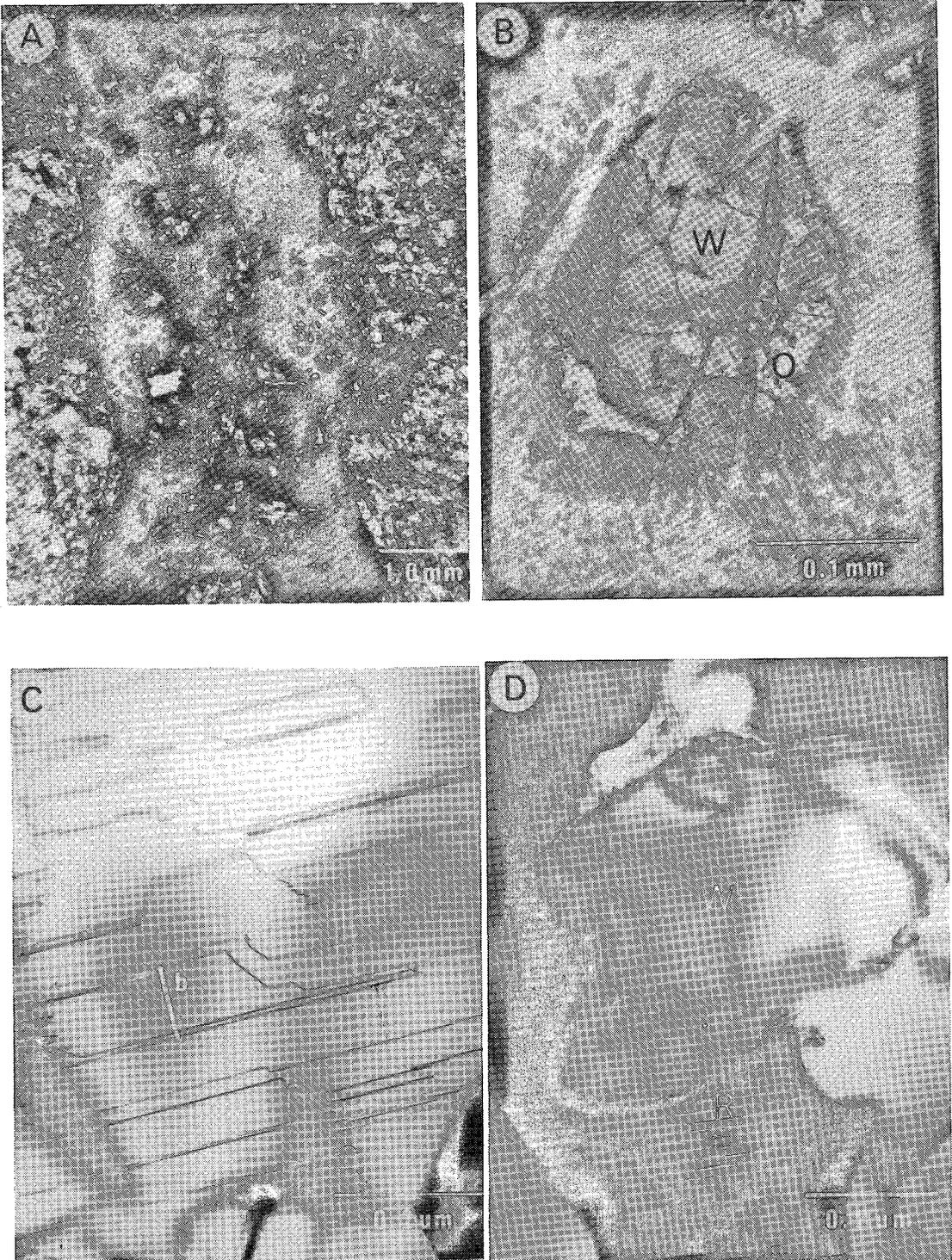


FIG. 1. A. Typical vein-structure in the Peace River meteorite. The light areas to the left and right of the vein are recrystallized chondrite of which the meteorite is largely composed. The opaque vein-material is made up of sulfide and metal droplets and microcrystalline silicate phases. The rounded fragments

investigations in minerals and inorganic compounds are renowned to all within his field and to many outside". We endorse this proposal, which has also been approved by the Commission on New Minerals and Mineral Names of the International Mineralogical Association. The type specimen is preserved in the collection of the Department of Geology, University of Alberta.

OCCURRENCE AND APPEARANCE

Wadsleyite has been found in the L6 hypersthene-olivine chondritic Peace River meteorite, the fall and recovery of which have been described by Folinsbee & Bayrock (1964). The Peace River meteorite is distinctly recrystallized, and has only a poorly preserved chondritic structure. The meteorite is largely an assemblage of olivine, orthopyroxene, plagioclase, iron-nickel alloys and troilite. The plagioclase has been extensively converted to its amorphous equivalent, maskelynite, which indicates that the meteorite has been subjected to a high-pressure shock event. In addition to this shock-produced phase, the Peace River meteorite contains thin, black, sulfide-rich veins, which pervade the body of the specimen in much the same way as veins found in other meteorites believed to have undergone an extraterrestrial shock event [*e.g.*, Tenham, Coorara, Catherwood and Coolamon: Price *et al.* (1979)]. Typically, within rounded fragments found in these veins, the constituent grains of olivine and orthopyroxene have been transformed into their high-density polymorphs, the spinel-structure ringwoodite and the garnet-structure majorite, respectively (*e.g.*, Binns 1970, Price *et al.* 1979). The vein studied in the Peace River meteorite differs significantly from those described in other meteorites, however, in that it contains significant quantities of wadsleyite.

The wadsleyite occurs as microcrystalline aggregates that pseudomorph previously existing olivine fragments within the vein (Figs. 1A, B). The wadsleyite-bearing fragments rarely exceed 0.5 mm in diameter, and the actual grain-size of the crystals within the polycrystalline fragments is between 0.5 and 5 μm , as estimated

by transmission electron microscopy (TEM). The polycrystalline aggregates of wadsleyite have a felsitic texture and are invariably fractured. They are transparent and have a pale fawn coloration. By virtue of the small crystal-size, no detailed optical data on wadsleyite could be obtained; however, the grains are anisotropic and show low, first-order birefringence colors. Relatively large wadsleyite aggregates have an effective index of refraction of 1.76. This compares well with the value of 1.77 calculated from the Gladstone-Dale rule (Mandarino 1976, 1978, 1979).

TEM shows that wadsleyite polycrystalline aggregates are generally composed of well-formed grains, with intergranular boundaries usually meeting at triple points (often with interfacial angles close to 120°). In addition to wadsleyite, the fragments may contain small amounts of majorite or microcrystalline aggregates of pyroxene pseudomorphing majorite (Price *et al.* 1979) and highly faulted ringwoodite. Wadsleyite is also occasionally found to carry stacking faults, which predominantly lie on (010) (Fig. 1C). These may be viewed as Frank-type faults, corresponding to the removal of a stoichiometric $(\text{Mg,Fe})_2\text{SiO}_4$ layer accompanied by a $\frac{1}{4}[010]$ displacement, and are interpreted as being structural mistakes incurred during the relatively rapid, post-shock growth process.

CHEMICAL AND STRUCTURAL DATA

Electron-microprobe data for olivine, wadsleyite and the other major, nonmetallic phases found in the Peace River meteorite are given in Table 1, and their recalculated structural formulae in Table 2. The analyses were performed using an ARL EMX microprobe fitted with three wavelength-dispersion spectrometers and an Ortec energy-dispersion spectrometer. Well-characterized analytical standards were used throughout. All data were obtained at an operating voltage of 15 kV and with probe currents of the order of 20 nA. Wavelength-dispersion results were processed using APL program PROBEDATA (Smith & Tomlinson 1970), and

within the vein are largely composed of shocked olivine and its high-density polymorphs, wadsleyite and ringwoodite. B. An enlarged view of a wadsleyite-bearing fragment surrounded by vein material. The fragment is made up of microcrystalline wadsleyite (W) and shocked olivine (O). The development of fracturing is common. C. Transmission electron micrograph of wadsleyite, showing stacking faults developed normal to (010). The faults have a displacement of $\frac{1}{4}[010]$. These faults occur in the wadsleyite because of the relatively rapid, post-shock growth process. D. Electron micrograph of a fault-free wadsleyite (W) grain topotactically replacing highly faulted ringwoodite (R). The two phases are related such that $[010]_W \parallel [110]_R$ and $[001]_W \parallel [001]_R$.

TABLE 1. COMPOSITIONS OF ANALYZED PHASES IN THE PEACE RIVER METEORITE

No. of Anal.	OLIVINE			WADSLEYITE			LOW-Ca PYROXENE			HIGH-Ca PYROXENE			'MAJORITE'		
	AV	HI	LO	AV	HI	LO	AV	HI	LO	AV	HI	LO	AV	HI	LO
H†															
F															
O*	40.82	40.91	40.74	40.91	41.06	40.81	44.60	44.72	44.38	43.60	43.79	43.52	44.25	44.71	43.46
Na										0.17	0.37	0.0			
Mg	23.15	23.29	22.99	23.05	23.53	22.74	17.26	17.61	17.03	10.19	10.56	10.05	17.78	18.59	17.35
Al	0.03	0.07	0.0				0.09	0.14	0.0	0.28	0.33	0.21	0.06	0.08	0.0
Si	17.87	17.93	17.76	18.08	18.25	17.97	25.97	26.21	25.53	25.27	25.40	25.16	25.24	26.05	23.73
P															
S															
Cl															
K															
Ca	0.01	0.06	0.0	0.05	0.11	0.0	0.53	0.70	0.41	15.42	15.82	15.10	0.42	0.57	0.28
Ti	0.0	0.0	0.0				0.09	0.12	0.0	0.25	0.27	0.21	0.10	0.11	0.09
V															
Cr	0.0	0.0	0.0	0.01	0.07	0.0	0.09	0.21	0.0	0.58	0.69	0.48	0.13	0.23	0.08
Mn	0.37	0.43	0.32	0.33	0.36	0.31	0.38	0.41	0.33	0.15	0.18	0.12	0.37	0.41	0.33
Fe	17.67	17.80	17.43	17.39	17.78	16.73	10.95	11.57	10.71	4.05	4.43	3.45	11.60	13.26	10.52
Co															
Ni	0.04	0.08	0.0	0.09	0.13	0.07	0.01	0.08	0.0	0.01	0.08	0.0	0.02	0.07	0.0
Zn	0.04	0.12	0.0	0.08	0.19	0.0	0.03	0.11	0.0	0.03	0.11	0.0	0.03	0.08	0.0
TOTAL	100.00	(*100.36)		100.00	(*100.62)		100.00	(*100.33)		100.00	(*100.05)		100.00	(*98.38)	

No. of Anal.	PLAGIOCLASE			CHROMITE			ILMENITE ^I			MERRILLITE ^I			APATITE ^I		
	AV	HI	LO	AV	HI	LO	AV	HI	LO	AV	HI	LO	AV	HI	LO
H†										0.07	0.18	0.0	0.04	0.08	0.0
F										0.37	0.40	0.34	1.01	1.05	0.97
O*	48.11	48.18	48.02	30.20	30.22	30.16	32.06	32.15	31.97	41.73	42.11	41.49	37.44	37.57	37.36
Na	7.03	7.34	6.08							1.98	2.04	1.81	0.38	0.40	0.36
Mg	0.23	0.41	0.10	1.88	2.06	1.72	1.75	1.88	1.61	2.36	2.49	2.29	0.39	0.39	0.39
Al	10.98	11.05	10.82	3.15	3.30	3.00				0.11	0.14	0.09	0.15	0.17	0.13
Si	30.48	30.55	30.38	0.44	0.54	0.40	0.26	0.35	0.18	0.24	0.32	0.18	0.30	0.35	0.25
P										19.73	19.88	19.40	17.65	17.69	17.65
S															
Cl													5.01	5.20	4.83
K	0.90	2.04	0.56												
Ca	1.60	1.80	1.44	0.02	0.12	0.0	0.04	0.04	0.03	32.69	32.93	32.17	37.37	37.58	37.21
Ti	0.0	0.0	0.0	1.77	1.90	1.59	30.62	31.29	29.96						
V				0.40	0.46	0.36									
Cr				36.88	37.26	36.08	0.17	0.28	0.06						
Mn	0.01	0.06	0.0	0.36	1.04	0.17	0.95	1.03	0.87	0.08	0.18	0.0	0.04	0.08	0.0
Fe	0.65	0.73	0.58	24.58	25.80	24.27	34.14	34.50	33.78	0.65	0.97	0.40	0.22	0.26	0.18
Co															
Ni							0.02	0.03	0.01						
Zn				0.32	0.42	0.26									
TOTAL	100.00	(*100.07)		100.00	(*100.09)		100.00	(*99.09)		100.00	(*100.05)		100.00	(*100.08)	

†H calculated from H₂O by difference from 100%

* Original totals from which analyses have been recalculated

‡ Wavelength dispersive analysis used for ilmenite and for F, Si & Fe on apatite and merrillite. All other determinations by energy-dispersive analysis.

*O calculated throughout

TABLE 2. STRUCTURAL FORMULAE OF PHASES IN PEACE RIVER METEORITE

	OLIVINE	WADSLLEYITE	LOW-Ca PYROXENE	HIGH-Ca PYROXENE	MAJORITE	PLAGIOCLASE	CHROMITE	ILMENITE	MERRILLITE	APATITE
H									1.4526	0.2158
F									0.4158	0.2737
O	4.0000	4.0000	6.0000	6.0000	6.0000	8.0000	32.0000	3.0000	56.5244	12.0326
Na				0.0160		0.7321			1.8620	0.0853
Mg	1.4931	1.4826	1.5277	0.9222	1.5871	0.0247	1.3774	0.1075	2.1036	0.0814
Al	0.0016		0.0071	0.0226	0.0051	1.0830	1.9760		0.0908	0.0289
Si	0.9978	1.0069	1.9905	1.9809	1.9488	2.8877	0.2655	0.0141	0.1878	0.0551
P									13.8016	2.9319
S										
Cl										
K						0.0614				0.7269
Ca		0.0018	0.0286	0.8472	0.0299	0.1064	0.0100	0.0013	17.6723	4.7941
Ti			0.0040	0.0114	0.0046		0.6256	0.9571		
V							0.1331			
Cr	0.0011	0.0004	0.0037	0.0245	0.0053		12.0240	0.0049		
Mn	0.0105	0.0095	0.0149	0.0060	0.0145	0.0002	0.1108	0.0258	0.0300	0.0035
Fe	0.4960	0.4871	0.4420	0.1597	0.4514	0.0310	7.4622	0.9153	0.2518	0.0202
Co										
Ni	0.0011	0.0024	0.0005	0.0003	0.0008			0.0006		
Zn	0.0011	0.0020	0.0011	0.0011	0.0008		0.0824			

energy-dispersion spectra by EDATA (Smith & Gold 1976) or EDATA2 (Smith & Gold 1979).

Analysis of five polycrystalline wadsleyite fragments gave an ideal formula of $Mg_{1.3}Fe_{0.5}SiO_4$. This composition is more iron-rich than that of previously reported synthetic β -(Mg,Fe) $_2$ SiO $_4$, and the observed wadsleyite may represent a metastable extension of the β -phase field. Untransformed olivine in the body of the meteorite was found to have the same composition (within experimental limits) as the wadsleyite (Table 1). The similarity in composition between these two polymorphs is consistent with the nonequilibrium, shock-induced nature of the transformation involved in the formation of the high-density (Mg,Fe) $_2$ SiO $_4$ phase. By analogy with ringwoodite, the spinel polymorph of (Mg,Fe) $_2$ SiO $_4$, it is suggested that the name *wadsleyite* should apply to all specimens with the β -phase structure in the system Mg $_2$ SiO $_4$ -Fe $_2$ SiO $_4$, in which Mg > Fe.

The compositions of the low- and high-Ca pyroxenes found in the body of the meteorite also are presented in Table 1. TEM reveals that adjacent to the shock-produced veins, the low-Ca pyroxenes occur both in monoclinic and orthorhombic forms. The monoclinic polymorph invariably exhibits polysynthetic twinning, suggesting that it has inverted from an earlier protopyroxene structure (*cf.* Price *et al.* 1979).

Compositions also are given for the plagioclase, chromite, ilmenite, merrillite, apatite and 'majorite' (or retrograded majorite) found in the meteorite.

Wadsleyite-containing fragments were hand-picked from the vein in the Peace River meteorite, and an X-ray powder pattern was obtained with a 114.6-mm-diameter Gandolfi camera. Owing to the fine-grained nature of the material, the diffraction peaks were necessarily broadened. Nevertheless, the sample yielded twelve well-defined powder lines (Table 3) that were all indexed in terms of the known β -phase structure (Moore & Smith 1970). A least-squares refinement of the wadsleyite X-ray data gave cell-parameter values for the orthorhombic lattice of a 5.70(2), b 11.51(7) and c 8.24(4) Å. The calculated cell-volume of wadsleyite is 541(3) Å 3 , and with $Z = 8$, the calculated density, on the basis of the idealized formula, is 3.84 g cm $^{-3}$. A recent structure determination of the synthetic β -Mg $_2$ SiO $_4$ polymorph (Horiuchi & Sawamoto 1981) has confirmed that β -Mg $_2$ SiO $_4$ has the *Imma* space group and cell parameters a 5.698, b 11.438, c 8.257 Å. Differences between these data and those obtained for wadsleyite are explainable in terms of the differing compositions of the phases and the relative precision of the two sets of data.

TABLE 3. X-RAY POWDER-DIFFRACTION DATA FOR WADSLLEYITE AND SYNTHETIC $\beta\text{-Mg}_2\text{SiO}_4$

WADSLLEYITE [†]				$\beta\text{-Mg}_2\text{SiO}_4$ [*]			
<u>I</u>	<u>do</u>	<u>dc</u>	<u>h k l</u>	<u>I</u>	<u>do</u>	<u>dc</u>	<u>h k l</u>
20	3.195	3.208	1 1 2	40	3.206	3.207	1 1 2
50	2.886	2.877	0 4 0	20	2.855	2.861	0 4 0
40	2.691	2.673	0 1 3	40	2.677	2.673	0 1 3
30	2.637	2.623	2 1 1	50	2.622	2.621	2 1 1
15	2.583	2.553	2 2 0	5	2.556	2.550	2 2 0
100	2.452	2.452	1 4 1	100	2.437	2.442	1 4 1
80	2.038	2.025	2 4 0	100	2.019	2.018	2 4 0
15	1.872	1.876	1 4 3	10	1.875	1.872	1 4 3
20	1.670	1.670	2 0 4	15	1.671	1.673	2 0 4
30	1.567	1.563	3 0 3	10	1.562	1.562	3 0 3
30	1.552	1.557	3 4 1	20	1.554	1.554	3 4 1
80	1.442	1.444	2 4 4	100	1.444	1.442	2 4 4

† CuK α radiation, Ni filtered; polycrystalline fragment, 114.6mm Gandolfi camera; intensities estimated visually; indices based on an orthorhombic cell, space group Imma.

* Data taken from Moore & Smith (1970)

PARAGENESIS

The occurrence of wadsleyite in the Peace River meteorite should be interpreted in terms of a general sequence of transformations, both prograde and retrograde, during a shock event. In the prograde sequence, high-density phases are formed in veins that have resulted from the interaction of shock-wave fronts passing irregularly through the polycrystalline parent body (Frederiksson *et al.* 1963). Within these veins, olivine is transformed to ringwoodite and pyroxene to majorite; both have apparently nucleated from a high-density glassy phase (Price *et al.* 1979). There is no evidence to suggest that wadsleyite forms as an intermediate between olivine and ringwoodite in this prograde sequence.

The retrograde sequence is the result of a post-shock thermal event (Stöffler 1972). A decrease in pressure coincides with a temperature increase, enabling lower-density phases to replace those formed during the peak pressure of the shock. The effect of this thermal event appears

to depend on the time scale over which it occurs. In the Tenham meteorite (Putnis & Price 1979, Price *et al.* 1979), the thermal event was relatively short, and little reversion to lower-density phases occurred. Thus, for example, majorite is found only partly retrograded to a microcrystalline aggregate of pyroxene. The pressure release causes stacking faults of the type $\frac{1}{4}$ [110] (110) to form in ringwoodite; these locally produce the cation distribution of wadsleyite in the plane of the fault.

The Peace River meteorite shows evidence of a longer retrograde event. The majorite is almost totally transformed to microcrystalline pyroxene, and the ringwoodite, where still preserved, has a very high density of stacking faults. Within these highly faulted regions, wadsleyite (Fig. 1D) is able to nucleate and topotactically replace the ringwoodite (Price *et al.* 1982). This sequence represents an example of a kinetically controlled transformation, in which wadsleyite is formed as an intermediate between ringwoodite and the ultimately stable, low-density olivine polymorph.

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