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X-RAY IDENTIFICATION OF ORDERED AND DISORDERED ORTHO-ENSTATITE

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ABSTRACT

Five meteoritic and three terrestrial ortho-enstatites have been examined using powder and single-crystal *x*-ray techniques. Geiger-counter intensity data are presented for two samples, one ordered and one disordered. Disordered ortho-enstatites were found in four of the meteoritic and none of the terrestrial samples. In the work to date (Brown and Smith, 1963, and the present paper) disordered ortho-enstatite has been detected in four enstatite achondrites, and found absent from three hypersthene and one pyroxene-plagioclase achondrite.

INTRODUCTION

Brown and Smith (1963) have shown from single-crystal studies that some of the enstatite in Norton County and Cumberland Falls meteorites is disordered parallel to the 18.2 Å axis or *a* axis. (In this paper the more common designation of the 18.2 axis as *a* and the 8.80 axis as *b* and the 5.18 axis as *c* will be followed.) They also found that the repeat along the *a* axis of the Cumberland Falls is not regular, and that the intensity and diffuseness of certain reflections is not uniform among all the disordered crystals.

Previous to the publication of Brown and Smith's paper we had begun a study of the variability of enstatites because of the discrepancy between the *X*-Ray Powder Data File data for the Bishopville enstatite and the pattern obtained from the Cumberland Falls meteorite. A sample of the Bamle, Norway, enstatite gave a pattern different from the other two. This led to the examination of other meteoritic and terrestrial enstatites using both single crystal and powder techniques.

The purposes of this paper are (1) to show the major differences between the powder patterns of enstatites showing disorder and those showing little or no disorder, (2) to present intensity data for an ordered and a disordered ortho-enstatite, and (3) to report the results from the study of five achondrites and three terrestrial ortho-enstatites.

EXPERIMENTAL

All powder and single-crystal *x*-ray work reported here was carried out using filtered copper radiation. Debye-Scherrer patterns were obtained with a Philips 114.6 mm diameter camera. A Philips diffractometer equipped with a Geiger-counter was used for the diffractometric studies.

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Intensity measurements were made by scanning over the samples at $\frac{1}{4}°$ per minute at various scale factors to maximize the size of the peaks. The intensities were then determined as follows. In the region of each peak the intensities were recorded as chart units every $\frac{1}{16}°$ 2θ ($\frac{1}{8}''$ on the chart). From previously calibrated charts these intensities were converted to counts per second and then corrected for dead time losses (Klug and Alexander, 1954). Background was also determined and subtracted from each point of the peak. The intensity for each peak was taken as the sum of the intensities above background. Visual inspection of the Debye-Scherrer films showed that the relative intensities were about the same as those determined with the diffractometer, indicating that little or no preferred orientation had occurred.

A sample of the Bamle enstatite was ground and fractionated to obtain the less-than-10-micron fraction. Insufficient Bishopville or Cumberland Falls enstatite was available to carry out a size separation, so these samples were ground until no grittiness was detected. Since intensity measurements of the two strongest peaks were reproducible to within 5%, we felt that the samples were in a suitable crystallite size range.

Samples for diffractometric study were packed in aluminum holders. Whenever sufficient sample was available to use a holder 21.0×10.5 mm, 1° divergent and scatter slits were used. However, whenever only small samples were available, $\frac{1}{2}°$ slits were used and a 10×10 mm holder was employed. An 0.006″ receiving slit and nickel filter were used at all times.

Powder Diffraction Studies

More information can usually be obtained from single-crystal photographs, especially where disorder is involved, than from Debye-Scherrer patterns. However, in this particular study, the powder method proved to be very useful. It enabled us to study a large number of samples with relative ease, and it provided information about the microcrystalline and irregularly-shaped fragments one would ordinarily not select for single-crystal work.

Figure 1 shows Debye-Scherrer patterns of two ordered (Bamle and North Carolina) and two disordered ortho-enstatites (Cumberland Falls and Norton County). The most striking differences between the patterns of the disordered Cumberland Falls and the ordered Bamle enstatites are shown more graphically in Fig. 2. Whereas the (410), (221) doublet is more intense than the (610) reflection in the Bamle, the reverse is true for the Cumberland Falls. The Cumberland Falls also shows an additional broad line at 2.96 Å, on the low-angle side of the (321) reflection, and what appears on this trace as an absence of the (421). Other differences between ordered and disordered enstatites, which can be seen on powder

patterns (Fig. 1), are a higher intensity of the line at about 4.43 Å for the disordered ones, and a change in the relative intensities of the six lines in the range 2.12 to 1.96 Å.

Table I lists the d spacings and intensities for a less than 10 micron fraction of Bamle enstatite. The d spacings were measured from the same samples used for intensity measurements. Calibration of the unit was achieved by measuring the d spacings for a quartz sample and deter-

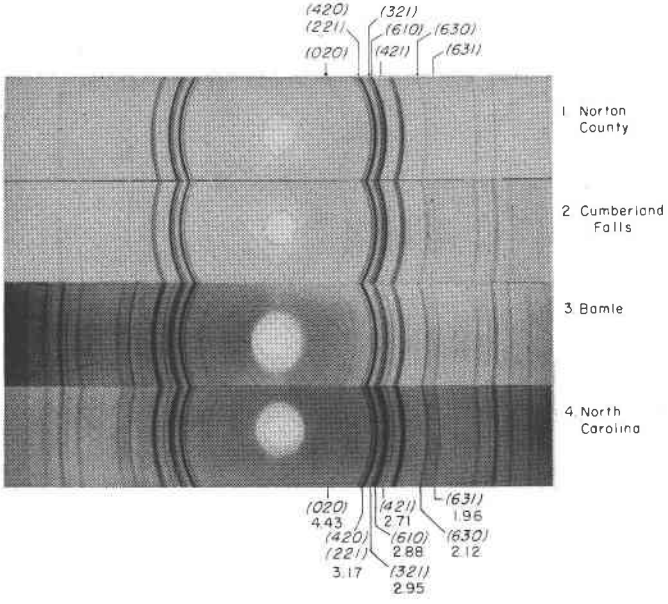

FIG. 1. Debye-Scherrer patterns of disordered 1, Norton County, and 2, Cumberland Falls 2; and ordered 3, Bamle, and 4, North Carolina ortho-enstatites.

mining the difference between the observed and calculated 2θ values. This correction was then applied to the measurements made on other samples. The d spacings of the Bamle enstatite are slightly larger than those measured for the Bishopville and this is probably due to a small amount of iron substituting for magnesium; refractive index measurements indicate 2 mole % $FeSiO_3$. There are probably very small amounts of biotite, talc and possibly augite in the Bamle sample.

Although intensity data for only one ordered ortho-enstatite, the Bamle, is presented here, powder patterns of North Carolina and New Mexico ortho-pyroxenes showed similar relative intensities. Table I also lists the data for the Bishopville enstatite from the *X*-Ray Powder Data File and from measurements made during the present work. The differ-

ences result from the use of two different methods of intensity measurements and also from the probability that the two samples are not identical. (In two separate samples of Bishopville, the integrated intensity of the (610) reflection was 61% and 75% of the (420), (221) doublet.) The data from the *X*-ray Powder Data File (Swanson *et al.*, 1956) was pre-

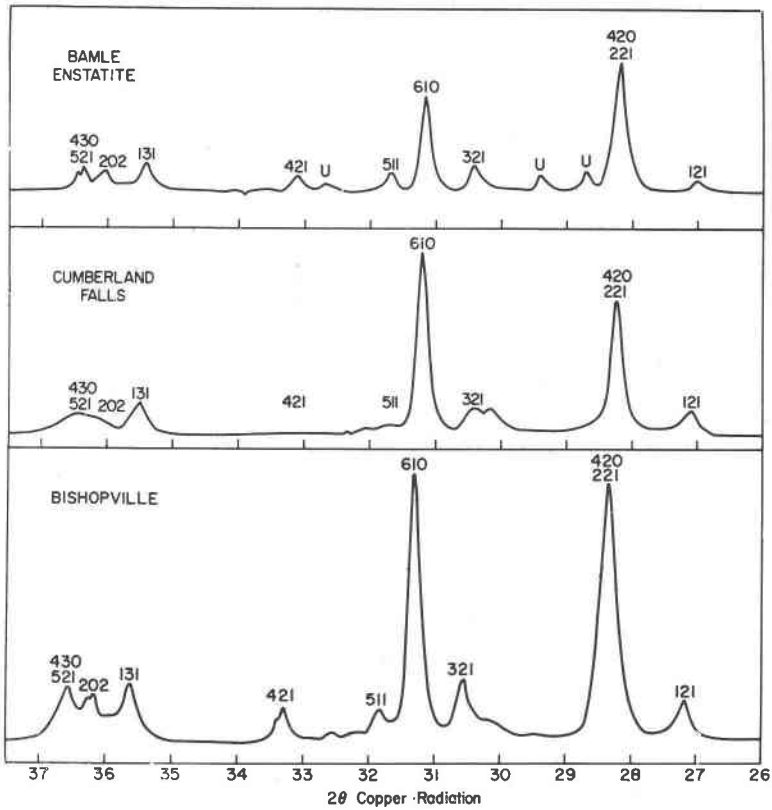

FIG. 2. Diffractometer traces of Bamle, Cumberland Falls, and Bishopville orthoenstatites, $2\theta = 26$ to 37°. CuKα radiation $\frac{1}{2}$° divergent and scatter slits, 0.006″ receiving slits, Geiger-counter detector. Automatic strip chart recorder scanning speed $\frac{1}{4}$° 2θ per min. Time constant, 2 seconds, Multiplier, 1, for Bamle and Cumberland Falls Scale Factor was 16, for Bishopville 8. U = lines from minerals other than enstatite.

pared using peak heights, while the present work makes use of integrated intensities. Intensity measured from peak height will be in fairly good agreement with the integrated intensity only when peaks are of equal breadth. For enstatite, the (420) and (221) reflections occur at slightly different values of 2θ; they cannot be resolved and appear to be a single

TABLE I. INTENSITY DATA FOR BAMLE, BISHOPVILLE AND CUMBERLAND FALLS ENSTATITES
CuK_{α_1}, $\lambda = 1.5405$ Å

hkl	Bishopville			Bamle		Cumberland Falls	
	d Å[1]	I/I_1 NBS*	I/I_1 This work	d Å	I/I_1	d Å	I/I_1
120	6.33	<1		6.33	<1	6.3	W
020, 111	4.41	14	7	4.43	3	4.41	8
211				4.028	1		W
121	3.303	35	11	3.314	6	3.30	15
				U 3.233	1		
420, 221	3.167	100	100	3.175	100	3.17	84
				U 3.122	2		
	2.96		6 B	U 3.049	5	2.96	28
321	2.941	44	18	2.946	16	2.94	
610	2.872	87	76	2.878	54	2.87	100
511	2.825	23	4	2.832	9	2.82	W
				U 2.746	2		
421	2.706	26	9	2.710	10	2.70	W, B
131	2.534	43	24	2.540	25	2.53	26
202	2.494	51	19	2.497	18	2.49	39
403, 521	2.471	31	19	2.477	18	2.47	
				U 2.386	<1		
331	2.358	7	N	2.364	1	2.36	W, B
			O	U 2.320	<1		
800	2.280	5	T	2.283	1	2.28	3
402, 711	2.252	7		2.257	3	2.24	W
431	2.232	7		2.239	3	2.22	W, B
630	2.114	24	M	2.116	12	2.11	21
531	2.096	21	E	2.100	12	2.09	
721, 512	2.058	13	A	2.060	5	2.05	10
820, 422	2.019	10	S	2.025	7	2.01	
421	1.984	13	U	1.988	9	1.98	7
631	1.958	24	R	1.961	11		
341, 612	1.926	4	E	1.929	1	1.92	W
821	1.887	6	D	1.888	4		
441, 332	1.854	3		1.841	4	1.85	W, B
622, 830	1.800	7		1.803	1		
640, 10.1.0	1.786	10		1.788	4	1.78	11
541	1.773	17		1.779	3	1.77	W, B
921	1.732	8		1.737	6	1.73	6
831	1.702	9		1.710	6		

[1] (Swanson *et al.*, 1956). U = lines from minerals other than enstatite. W = weak lines seen easier on photographs. B = broad lines.

TABLE 1—(*continued*)

hkl	Bishopville			Bamle		Cumberland Falls	
	d Å[1]	I/I_1 NBS*	I/I_1 This work	d Å	I/I_1	d Å	I/I_1
821, 142	1.679	9		1.681	1	1.67	W, B
741	1.649	7		1.652	1	1.64	W, B
10.2.1	1.603	20		1.610	11	1.60	14
931	1.588	10		1.591	6	1.58	7
551	1.525	7		1.529	5	1.53	15
12.0.0	1.520	14	10	1.522	7	1.52	
10.3.1	1.485	34	21	1.488	23	1.49	12
060, 642	1.470	22	17	1.473	17	1.47	21

diffraction maximum slightly broader than the (610) reflection. In Fig. 2 the widths at half-maximum of the (420), (221) doublet and (610) line are 0.22 and 0.18° 2θ, respectively, for the Bamle and for the Bishopville, 0.30 and 0.20° 2θ. Thus, using only the peak height of the (420), (221) line leads to an underestimation of its intensity which may range from moderate to serious. When the integrated intensities of the Bishopville sample were measured, most, but not all, of the relative intensities were found to be similar to those of the Bamle. The most evident exception is the (610) peak, which appears too intense. A third sample of Bishopville (a crystal about 1 mm^3) gave a powder photograph very similar to that of the Bamle. This indicated that the first Bishopville specimen is a mixture of ordered enstatite and a second phase.

The relative intensities of the two strongest lines, and the appearance of a broad, weak line at 2.96 Å on the Bishopville pattern are the main evidences that the second phase is disordered ortho-enstatite. The ratio of the intensities of the (610) and the (420), (221) reflections is 0.76, compared to the 0.54 for the Bamle and 1.19 for Cumberland Falls. Six Bishopville single crystals were examined; five were definitely ordered and the sixth crystal was really an aggregate, so no conclusion was reached concerning it. Even though no individual disordered Bishopville crystals have been observed, the powder data indicate they are there, if not as macroscopic crystals, then as microscopic ones.

The first meteorite shown to contain ordered and disordered ortho-enstatite was the Norton County specimen, which Brown and Smith (1963) studied using single-crystal techniques. In the present work the two single-crystals of Norton County enstatite that were examined were disordered, while powder patterns of the bulk sample indicated it was a mixture of ordered and disordered ortho-enstatite. Four samples have

been taken from one large shattered crystal of the Norton County enstatite and all have been disordered. It is hoped that this crystal will prove useful in correlating optical properties with disorder as determined by x-ray diffraction. The d spacings of the Cumberland Falls pattern in Fig. 1 are slightly larger than those of the Norton County, but the intensities are almost identical.

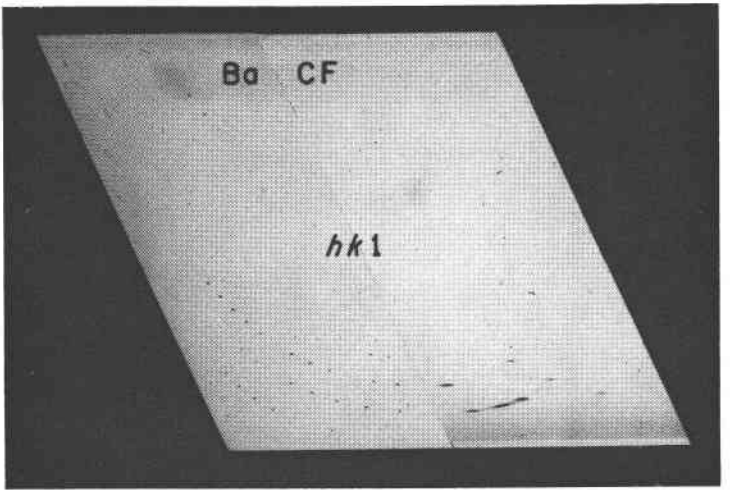

FIG. 3. Weissenberg photograph containing ($hk1$) net of ordered Bamle (Ba) and disordered Cumberland Falls (CF) crystals.

SINGLE-CRYSTAL DIFFRACTION STUDIES

The Weissenberg single-crystal technique was the most useful one in this work. Most samples were mounted with c as the oscillation axis since the fragments usually had this axis as the longest direction. Crystals with the longest dimension 0.2 to 0.4 mm were used for the most part, because in the meteorite samples at our disposal most of the fragments larger than about 0.2 mm were aggregates of split crystals. As mentioned by Brown and Smith (1963), the diffuse reflections only occur for reflections where $l \neq 0$; therefore the ($hk0$) net cannot be used to tell if disorder is present. The disorder is easily seen on photographs of the Cumberland Falls (Fig. 3) and Pesyanoe meteorites, where, all reflections ($hk1$) with h even are diffuse and reflections ($hk2$) with h odd are diffuse. For the Norton County disordered crystals (Fig. 4) the same classes of spots appear diffuse; however, the sharp spots are split, giving rise to an enlarged a axis. An a axis of about 91 Å was calculated from measurements made on a precession photograph containing the ($h1l$) net.

There is some indication that the Cumberland Falls crystals display

the same splitting as the Norton County, but most spots are too diffuse to be resolved. An example of this is the (321) reflection. On Norton County Weissenberg photographs a splitting of this reflection occurs, but on the Cumberland Falls photograph the splitting cannot be detected. However, the Debye-Scherrer patterns of both specimens and the diffractometer trace of the Cumberland Falls in Fig. 2 all show a broad line indicating a doublet. Only on small regions of the (*hk*1) and (*hk*2) photo-

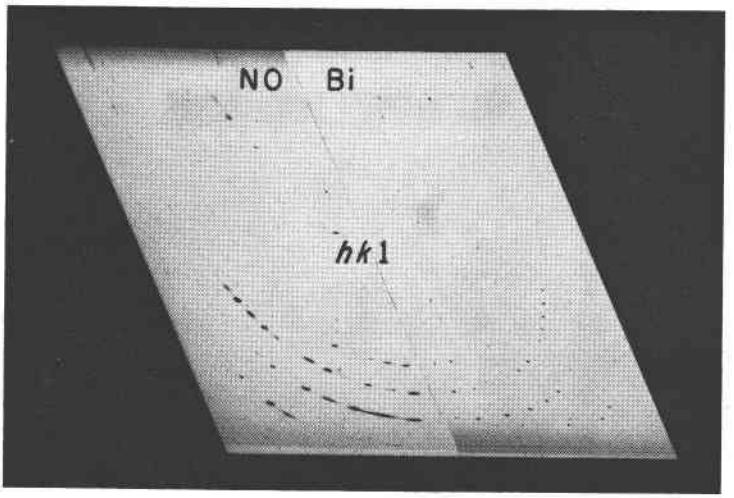

FIG. 4. Weissenberg photograph containing (*hk*1) net of ordered Bishopville (Bi) and disordered Norton County (NO) crystals.

graphs of the Cumberland Falls photographs can splitting identical with that of the Norton County be seen.

Table II contains unit cell dimensions and estimates of the mole fraction of $MgSiO_3$, showing that all the samples studied fall in the enstatite-bronzite range of ortho-pyroxenes. No diffuse spots were observed on the patterns of the terrestrial samples.

DISCUSSION

The intensity data just presented for ordered and disordered enstatites should make their identification easier. Probably the best method of identifying a powdered sample is to have reference Debye-Scherrer patterns of ordered and disordered enstatites to compare with the pattern of a sample in question. No attempt at quantitative estimation of the disordered enstatites in the samples has been made, and it is not worthwhile until the uniformity of their patterns is established. In this work the powder patterns of two, Norton County and Cumberland Falls, were

shown to be nearly alike. No way has been found of isolating the disordered portion of the Bishopville specimen, and the Pesyanoe sample was limited to three tiny crystals.

Table III summarizes the occurrence of disordered ortho-enstatites as recorded by Brown and Smith (1963) and in the present study. Although the actual weight fraction of the meteorites studied was exceedingly small, two results emerge, (1) all four of the enstatite achondrites which have been investigated contain disordered ortho-enstatite and (2) none of the three hypersthene achondrites investigated contain disordered orthopyroxene. Further study on more representative samples may indeed show that disordered ortho-pyroxene is present in the hypersthene achondrites listed in Table III.

TABLE II. UNIT CELL DIMENSIONS FROM SINGLE-CRYSTALS
CuK_{α_1}, $\lambda = 1.5405$ Å

Sample	a(Å)	b(Å)	c(Å)	Mole %[1] $MgSiO_3$
Bishopville	18.217±0.009	8.816±0.005	5.180±0.005	100
Bamle	18.230±0.009	8.840±0.005	5.188±0.005	98
New Mexico	18.238±0.009	8.801±0.005	5.200±0.005	89
North Carolina	18.230±0.009	8.823±0.005	5.188±0.005	93
Norton County (Disordered)	~91	8.81 ±0.05	5.15 ±0.1	100
Cumberland Falls (Disordered)	?	8.81 ±0.05	5.15 ±0.1	100
Tatohouine	Not Measured			77
Pesyanoe	Not Measured			100

[1] Estimated from γ refractive index by Arch Reid.

The distribution of disordered ortho-pyroxenes should prove useful in showing further differences or similarities among the stony meteorites. A comprehensive study is needed, however, before its significance can be evaluated.

ACKNOWLEDGMENTS

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TABLE III. SUMMARY OF ORDER AND DISORDER IN ACHONDRITES THAT HAVE BEEN EXAMINED

Sample	Pyroxene Polymorphs Identified	Workers	Type of Achondrite
Bishopville, S. Car.	ortho-pyroxene (5 crystals)	BS	Enstatite
	ortho-pyroxene (5 crystals)	This work	
	ortho and disordered-ortho-pyroxene (ground powder)	This work	
Cumberland Falls, Ky.	disordered-ortho-pyroxene (2 crystals)	BS	Enstatite
	disordered-ortho-pyroxene (2 crystals)	This work	
Johnstown, Colorado	ortho-enstatite (3 crystals)	BS	Hypersthene
Juvinas, France	ortho-pyroxene (1 crystal)	BS	Pyroxene-Plagioclase
	twinned clino-enstatite (1 crystal)	BS	
Norton County, Kansas	ortho-pyroxene (4 crystals)	BS	Enstatite
	disordered-ortho-pyroxene (7 crystals)	BS	
	disordered-ortho-pyroxene (2 crystals)	This work	
	ortho and disordered-ortho pyroxene (ground powder)	This work	
Pesyanoe, U.S.S.R.	disordered-ortho-pyroxene (1 crystal)	This work	Enstatite
Shalka, India	ortho-pyroxene (3 crystals)	BS	Hypersthene
Tatohouine, Tunisia	ortho-pyroxene (1 crystal and ground powder)	This work	Hypersthene

BS = Brown and Smith (1963)

versity of New Mexico (Norton County). The Cumberland Falls meteorite was provided by the Department of Geology, University of Miami. Oxford, Ohio, through the courtesy of T. E. Bunch of Mellon Institute. J. L. Carter of Rice University supplied the ortho-pyroxene from Kilbourne, New Mexico.

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