

UNIT-CELL PARAMETERS OF SYNTHETIC DIOPSIDE- HEDENBERGITE SOLID SOLUTIONS

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ABSTRACT

Unit-cell parameters for synthetic members of the diopside-hedenbergite series have been determined by least-squares refinement for 26 samples consisting of 11 compositions. Within the experimental error, the cell volume and cell edges a and b appear to change linearly over the entire compositional interval, although β does not. The c dimension is not sensitive to the Mg/Fe ratio. No significant difference was observed for samples synthesized on different oxygen buffers.

Four reflections were used to test the validity of a spacing curve for estimating the composition of clinopyroxenes from calc-silicate skarns. Eight samples from Willsboro, New York indicate that the composition of clinopyroxenes coexisting with wollastonite and garnet can be estimated to within ± 5 mole percent if elements other than Ca, Fe, Mg, Si, and O are known to be present in only very low concentrations.

INTRODUCTION

The relation between the chemical composition and the unit cell for the diopside-hedenbergite ($\text{CaMgSi}_2\text{O}_6$ - $\text{CaFeSi}_2\text{O}_6$) series has been the subject of several investigations, many of which are reviewed by Viswanathan (1966). Since most of the published data are for natural samples which do not adequately cover the entire compositional interval, do not have a constant $\text{Ca}/(\text{Mg}+\text{Fe})$ atomic ratio, and contain varying amounts of impurities, we have prepared synthetic samples in order to define this relation more accurately.

EXPERIMENTAL METHODS

Starting materials were reagent grade MgO , Fe_2O_3 , CaCO_3 , and floated silica powder or silicic acid which were carefully dehydrated before weighing. These materials in the desired proportions were mixed for three hours in a mechanical shaker, fired in air at approximately 950°C for fifteen minutes in a silver-foil lined silica-glass boat, and hand ground in an agate mortar for approximately one hour. Eleven compositions were prepared in this manner and samples of the mixes were used for synthesis. Replicate mixes of the 41.1 mole percent hedenbergite were prepared to check the reproducibility of the above method.

Synthesis was carried out in "cold-seal" pressure vessels using the oxygen buffer technique of Eugster and Wones (1962). Most of the runs were made in platinum tubes with silver foil around the charge to minimize iron loss. Some runs were made using $\text{Ag}_{70}\text{Pd}_{30}$ tubing (Muan, 1963). All of the runs were made between 725°C and 750°C and 1 Kb water pressure at the oxygen fugacity of the buffer indicated in Table 1. The only exception to this is the one run on the hematite-magnetite buffer which was done at 600°C . Run duration was from seven to fourteen days. Only runs that showed negligible weight change, maintenance of the buffer at the end of the run, and at least 98 weight percent clinopyroxene yield (traces of quartz and wollastonite were observed) were considered successful.

TABLE 1. CELL PARAMETERS AND OPTICAL DATA FOR DIOPSIDE-HEDENBERGITE SERIES

Run Number	Comp. Mole % hcd.	No. Lines Measured	a Å	b Å	c Å	β deg-min	V Å ³	α	γ	Buffer
WD 145	100	15	9.866±0.004	9.025±0.002	5.225±0.006	104 41.6±1.8	450.04±0.35	---	---	QFM
WD 217	100	14	9.852±0.003	9.025±0.002	5.247±0.003	104 46.3±1.4	451.16±0.19	1.733±0.003	1.758±0.003	QFM
WD 187	100	14	9.857±0.005	9.026±0.003	5.227±0.007	104 42.9±2.4	449.81±0.44	1.733±0.003	1.758±0.003	QFM
WD 240	100	15	9.847±0.003	9.024±0.002	5.242±0.002	104 46.2±1.2	450.36±0.15	1.733±0.003	1.758±0.003	NNO
WD 169	100	14	9.850±0.004	9.028±0.003	5.230±0.006	104 45.1±1.8	449.69±0.36	1.735±0.005	1.758±0.003	MW
WD 238	85.0	15	9.834±0.003	9.010±0.002	5.240±0.003	104 57.3±1.4	449.15±0.17	1.725±0.005	1.745±0.005	QFM
WD 126	68.2	10	9.816±0.004	8.987±0.003	5.252±0.003	105 4.4±3.6	447.41±0.28	---	---	QFM
WD 166A	68.2	13	9.816±0.003	8.991±0.002	5.253±0.002	105 5.7±1.9	447.61±0.19	1.710±0.005	1.740±0.005	QFM
WD 186	52.3	15	9.802±0.002	8.976±0.001	5.254±0.001	105 24.0±1.3	445.69±0.10	1.696±0.004	1.725±0.005	QFM
WD 167	52.3	13	9.801±0.003	8.974±0.002	5.248±0.003	105 27.8±1.4	444.92±0.16	1.698±0.002	1.730±0.005	QFM
WD 162	41.1	14	9.794±0.003	8.963±0.003	5.249±0.006	105 28.9±2.2	444.00±0.45	1.696±0.002	1.725±0.005	QFM
WD 163	41.1	16	9.789±0.002	8.960±0.001	5.251±0.002	105 29.1±1.3	443.85±0.17	1.692±0.002	1.720±0.005	QFM
WD 232	41.1	15	9.794±0.002	8.966±0.002	5.257±0.003	105 28.1±1.7	444.94±0.21	---	---	IW
WD 161	28.3	16	9.782±0.004	8.952±0.003	5.255±0.005	105 35.9±2.6	443.23±0.35	1.680±0.002	1.715±0.005	QFM
WD 123	28.3	15	9.782±0.003	8.960±0.003	5.243±0.005	105 35.3±1.9	442.66±0.31	---	---	QFM
WD 160	20.4	17	9.771±0.003	8.946±0.002	5.253±0.003	105 39.8±1.6	442.08±0.21	---	---	QFM
WD 144A	20.4	15	9.772±0.005	8.945±0.004	5.253±0.005	105 38.9±3.0	442.15±0.36	---	---	QFM
WD 130	20.4	15	9.774±0.003	8.944±0.002	5.249±0.003	105 38.4±1.4	441.88±0.22	1.676±0.002	1.715±0.005	QFM
WD 190	13.9	17	9.770±0.004	8.943±0.003	5.252±0.004	105 41.3±1.8	441.75±0.24	1.668±0.002	1.705±0.005	QFM
WD 159	7.9	16	9.772±0.006	8.934±0.006	5.253±0.007	105 45.8±3.7	441.32±0.47	---	---	QFM
WD 129A	7.9	15	9.767±0.004	8.936±0.003	5.246±0.006	105 40.8±2.2	440.84±0.35	---	---	QFM
WD 137	7.9	15	9.775±0.003	8.936±0.002	5.244±0.003	105 44.3±1.3	440.91±0.23	---	---	HM
WD 191	5.9	17	9.757±0.002	8.937±0.002	5.245±0.001	105 49.1±1.3	440.05±0.13	1.664±0.002	1.705±0.005	QFM
WD 170	0.0	17	9.750±0.005	8.927±0.004	5.254±0.006	105 47.6±3.0	439.99±0.40	---	---	---
WD 98C	0.0	14	9.755±0.005	8.926±0.003	5.241±0.009	105 50.5±4.0	439.04±0.64	1.660±0.002	1.698±0.002	---
WD 222	0.0	16	9.754±0.003	8.933±0.002	5.252±0.002	105 50.5±2.1	440.22±0.28	1.658±0.004	1.690±0.002	---

Smear mounts were prepared using reagent grade KCl, which had previously been standardized with Lake Toxaway quartz ($a=4.9131 \text{ \AA}$ and $c=5.4046 \text{ \AA}$) and silicon ($a=5.4306 \text{ \AA}$), as an internal standard. Two or four oscillations were made over the ranges $26-36^\circ$, $38-45^\circ$, and $49-52.5^\circ 2\theta$ using a goniometer speed of $1/4^\circ 2\theta$ per minute and chart speed of $1/2$ in. per minute. The goniometer was equipped with a curved crystal monochromator which gave an excellent peak to background ratio with copper radiation ($\text{CuK}\alpha=1.5418 \text{ \AA}$). The average deviation of four or eight individual measurements from the mean was between 0.01° and $0.02^\circ 2\theta$.

All members of the series were indexed using the space group $C2/c$. A least-squares refinement of the cell data was performed with the computer program written by Evans, Appleman, Handwerker (1963).

Ten to seventeen reflections were used for each refinement and the indices of the following reflections were fixed: (220) (221), (310), ($\bar{1}$ 31), (13 $\bar{1}$), (311), (330), (33 $\bar{1}$), (42 $\bar{1}$), and (150).¹ The errors reported here are the standard errors calculated by this program and give some indication of internal consistency of the measured 2θ values.

RESULTS

The cell parameters for a total of 26 samples and α and γ refractive indices for most of these are listed in Table 1. Cell parameters and cell volumes for all samples synthesized on the QFM buffer are shown in Figure 1. The volume and unit cell edges a and b appear to be linear over the entire interval, although β is not. The c dimension is not sensitive to the Mg/Fe ratio. An equation for the volume dependence on composition was calculated using York's (1966) "least-squares cubic" computer program. The assigned errors in this program were the standard errors calculated from the least squares program for the cell refinement and a compositional error estimated as ± 0.2 mole percent for all samples. The equation is:

$$V = 439.68 \pm 0.15 + (0.1110 \pm 0.0028)x \quad (1)$$

where V is in \AA^3 and X is mole percent hedenbergite. An F test (Snedecor, 1946, p. 382) indicates that the deviation from linearity is not significant. The probability is 0.3 that the deviation is due to random sampling error. Thus the solid solution appears to be ideal within the accuracy of these data. Kretz (1963) has also concluded that the calcium-rich clinopyroxenes are approximately ideal on the basis of element partitioning data for natural samples.

Within experimental error there is no difference in the cell parameters for identical compositions synthesized from different starting materials and on the oxygen buffers used in this study. However, bulk compositions more iron-rich than approximately 10 mole percent hedenbergite yield

¹ To obtain a copy of the table listing measured d values, order NAPS Document No. 00180 from ASIS National Auxiliary Publications Service, c/o CCM Information Sciences, Inc., 22 West 34th Street, New York, New York 10001; remitting \$1.00 for microfiche or \$3.00 for photocopies.

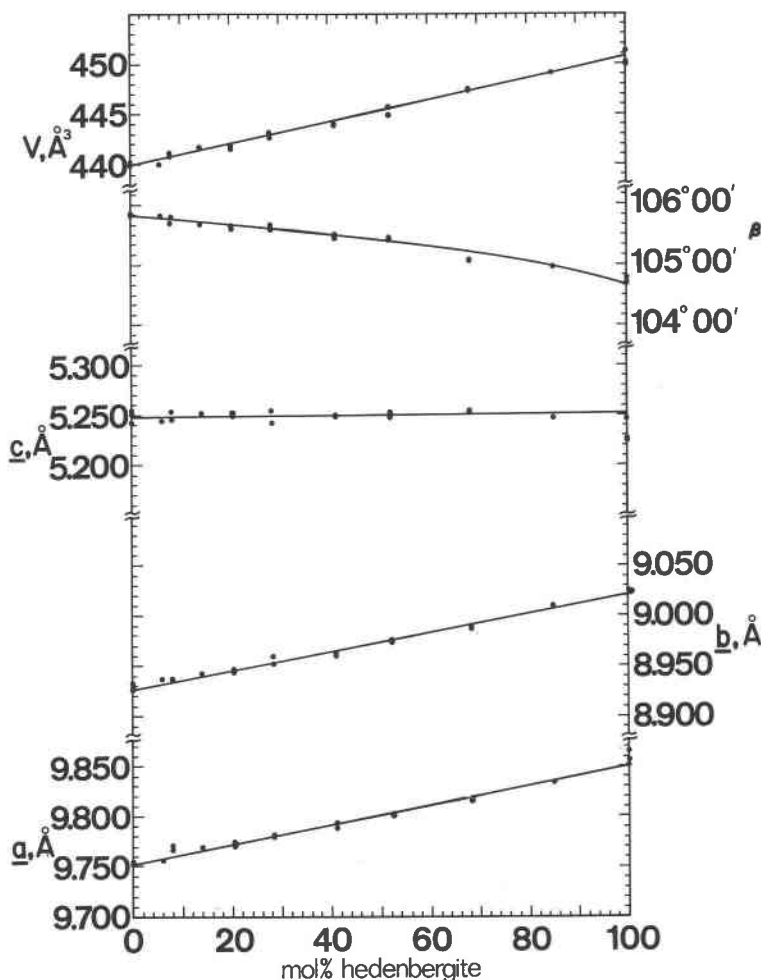


FIG. 1. Unit-cell parameters a , b , c , β and volume for the series $\text{CaMgSi}_2\text{O}_8$ - $\text{CaFeSi}_2\text{O}_6$ synthesized on the QFM buffer. Data from Table 1.

andraditic garnet and other phases in addition to a clinopyroxene on the hematite-magnetite buffer at 600°C and 1 kbar.

The cell parameters for the end members are compared with published values in Table 2. The absolute error in c is probably larger than the error in either a or b because of the sparsity of unambiguous indices with l greater than one. The values for a , b , and c in Table 2 are calculated from the least-square equations shown on Figure 1. The difference between these values and the average of the three determinations for each end

TABLE 2. COMPARISON OF CELL PARAMETERS FOR DIOPSIDE AND HEDENBERGITE

Material	Reference	a Å	b Å	c Å	β
Synth. Diopside ^a	This study	9.752	8.926	5.248	105°50'
		±0.002	±0.002	±0.002	
Synth. Diopside ^a	Clark, <i>et al.</i> (1962)	9.745	8.925	5.248	105°52'
		±0.001	±0.001	±0.001	
Synth. Diopside ^a	Sakata (1957)	9.743	8.923	5.251	105°56'
Synth. Diopside ^a	Nolan and Edgar (1963)	9.748	8.924	5.251	105°47'
Diopside ^b	Viswanathan (1966)	9.754	8.916	5.249	105°49'
		±0.014	±0.008	±0.009	
Synth. hedenbergite ^a	This Study	9.851	9.021	5.252	104°44'
		±0.004	±0.004	±0.004	
Hedenbergite ^b	Viswanathan (1966)	9.821	9.036	5.249	104°38'
		±0.012	±0.007	±0.008	
Herault hedenbergite	Kuno and Hess (1953)	9.854	9.024	5.263	104°20'

^a Calculated from least-squares equations for the QFM data in Table 1.

^b Extrapolated from intermediate compositions of natural samples.

member (Table 1) is small except for c of hedenbergite. Because of the large variation in the three values of c for hedenbergite in Table 1 and the larger inherent error mentioned above, we believe the value from the least-square equation is preferred.

The data for diopside is in good agreement with the published data, except our value for a is larger. We are not aware of any published cell data for synthetic hedenbergite and intermediate compositions. Viswanathan's (1966) values for pure hedenbergite extrapolated from natural samples are only in fair agreement with the values determined in this study (Table 2). The cell parameters for natural hedenbergite from Herault, California (Kuno and Hess, 1953) are included in Table 2 for comparison.

Indices of refraction of some of the samples were measured in white light. Only maximum and minimum indices could be determined for compositions because of the small grain size. Within the limits of measurement, α and γ are both linear over the entire compositional interval. The best straight line for these data using York's (1966) program are given by

$$\alpha = 1.660 \pm 0.001 + (0.000746 \pm 0.00002)x \quad (2)$$

and

$$\gamma = 1.695 \pm 0.001 + (0.00630 \pm 0.00003)x \quad (3)$$

where x is mole percent hedenbergite. These curves are in good agreement with the data summarized by Deer, Howie, and Zussman (1963).

APPLICATIONS

While it is realized that the great variability in composition of natural clinopyroxenes precludes a unique determination of their compositions from d -values, it is possible to estimate the composition of clinopyroxenes which are known to lie close to the diopside-hedenbergite join. Clinopyroxenes from calc-silicate skarns often fulfill this requirement. To test the validity of an X-ray spacing curve for determining the composition of such clinopyroxenes, samples consisting of essentially clinopyroxene, grossularite-andradite garnet, and wollastonite from Willsboro, New York were selected for analysis. The clinopyroxenes from these samples had previously been analyzed by X-ray fluorescence for total iron as part of a study to examine element partitioning between coexisting phases. The methods and results of this study will be published elsewhere.

The measured values for $d(220)$, $d(310)$, $d(131)$, and $d(150)$ from the samples synthesized on the QFM buffer (Table 1) were used to establish spacing curves. The variation of these d values with composition is linear, or very nearly so, and the "least-squares cubic" equations, where x is mole percent hedenbergite, are given below:

$$d(220) = 3.2329 \pm 0.0003 + (0.000416 \pm 0.000012)x \quad (4)$$

$$d(310) = 2.9505 \pm 0.0002 + (0.000439 \pm 0.000018)x \quad (5)$$

$$d(13\bar{1}) = 2.5640 \pm 0.0002 + (0.000206 \pm 0.000014)x \quad (6)$$

$$d(150) = 1.7538 \pm 0.0002 + (0.000194 \pm 0.000003)x \quad (7)$$

The relation for $d(310)$ is based on data from 0 to 68.2 mole percent hedenbergite because for more iron-rich compositions this reflection merges with the $(22\bar{1})$ reflection and cannot be measured accurately. The data for $d(13\bar{1})$ are only linear from 0 to 52.3 mole percent hedenbergite and equation (6) should not be used for more iron-rich composition. Equations (4) and (7) are valid over the entire compositional interval.

The compositions of eight clinopyroxenes from Willsboro, New York were determined from the above relations by measuring two oscillations for the (310) , $(13\bar{1})$, and (220) reflections and three for the (150) reflections. The clinopyroxene compositions as determined from these reflections are listed in Table 3 along with the compositions determined by X-ray fluorescence analysis for total iron.

The average composition determined from the d values agrees with the X-ray fluorescence analysis to within ± 3.4 mole percent hedenbergite except for sample MSR-12 which differs by 7.0 mole percent. This sample,

TABLE 3. COMPOSITION OF CLINOPYROXENES FROM WILLSBORO, N. Y.

Sample no.	Mole % hedenbergite determined from					
	<i>d</i> (220)	<i>d</i> (310)	<i>d</i> (13 $\bar{1}$)	<i>d</i> (150)	Average of <i>d</i> values	X-ray fluorescence
MSR 17	37.5	39.9	38.3	37.6	38.3	38.4
MSR 21B	24.8	25.1	26.2	24.2	25.1	24.3
MSR 37B	31.0	32.8	29.6	27.8	30.3	28.2
MSR 22A	20.9	23.2	23.8	21.6	22.4	22.5
MSR 29A	33.9	36.0	34.0	34.0	34.5	32.6
MSR 20	39.4	41.7	34.5	39.7	38.8	35.4
MSR 38C	34.9	34.4	34.0	38.1	35.3	33.6
MSR 12	20.9	20.3	18.4	16.5	19.0	26.0

unlike the others, is from a sphene and apatite-rich layer. The larger difference is probably due to titanium in the clinopyroxene.

These data indicate that the composition of clinopyroxenes coexisting with wollastonite can be approximately determined from equations (4) through (7) and probably to within ± 5 mole percent if other elements are known to be present in only very low concentrations.

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