

A LABORATORY RECONNAISSANCE OF THE LIQUIDUS SURFACE IN THE PYROXENE SYSTEM En-Di-Hd-Fs
(MgSiO_3 - $\text{CaMgSi}_2\text{O}_6$ - $\text{CaFeSi}_2\text{O}_6$ - FeSiO_3)

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ABSTRACT

Thirty-four relatively homogeneous synthetic glasses, melted in metallic iron crucibles in nitrogen at 1 atm., were made to fall as close as possible to the pyroxene quadrilateral plane in the system MgO-CaO-FeO-SiO_2 . As exact control by synthesis of the total FeO content is impossible, the glasses were analyzed, corrected by minor additions, re-fused, and reanalyzed. Phase equilibrium quenching runs were made on these glasses, in pure iron foil envelopes, to determine the general shape of the liquidus surface. Although the data are fragmentary, the major phase boundaries can be drawn with moderate accuracy. A quaternary liquidus field of olivine solid solutions extends into the system to a maximum Fs content of ~ 35 mole per cent and a minimum En content of ~ 41 mole per cent. The steep liquidus for silica (also quaternary equilibrium) includes all of the diagram above ~ 53 - 59 mole per cent Fs. The ternary undifferentiated liquidus for pyroxenes (and presumably wollastonite) is a shallow trough with lowest temperatures near hedanbergite; the solidus is rather close beneath.

INTRODUCTION

The pyroxene system En-Di-Hd-Fs, hereafter called the "pyroxene quadrilateral," is a plane through the more general system MgO-CaO-FeO-SiO_2 (Fig. 1). In 1951 the writer started a reconnaissance of the liquidus surface in this system, using synthetic batches run in pure nitrogen at one atmosphere, in equilibrium with metallic iron. Thirty-four compositions were made, a limited number of phase equilibrium quenching runs were made, and a tentative diagram, essentially as given here, was presented at a regional meeting of the Geological Society of America in Salt Lake City, Utah, in 1952 (Roedder, 1952b). This work was undertaken at the University of Utah, with the aid of a research contract from the Office of Naval Research. It was then put aside in the vain hope that it would serve as a starting point for graduate theses, either on portions of the pyroxene system itself, or, with the addition of water under pressure to specific compositions, on the amphiboles.² For various reasons the work was never extended much beyond this brief reconnaissance. Recently Yoder *et al.* (1963) have been making a thorough investigation of the pyroxenes at the Geophysical Laboratory, and have suggested that the earlier work of the author should be reported more fully, even though it is fragmentary.

¹ Publication authorized by the Director, U. S. Geological Survey.

² Some of the synthetic crystalline Mg-Ca-Fe pyroxenes made were found to react with water, in days, to form, among other things, asbestiform amphibole-like phases ($\sim 15,000$ psi and 300 - 400°C).

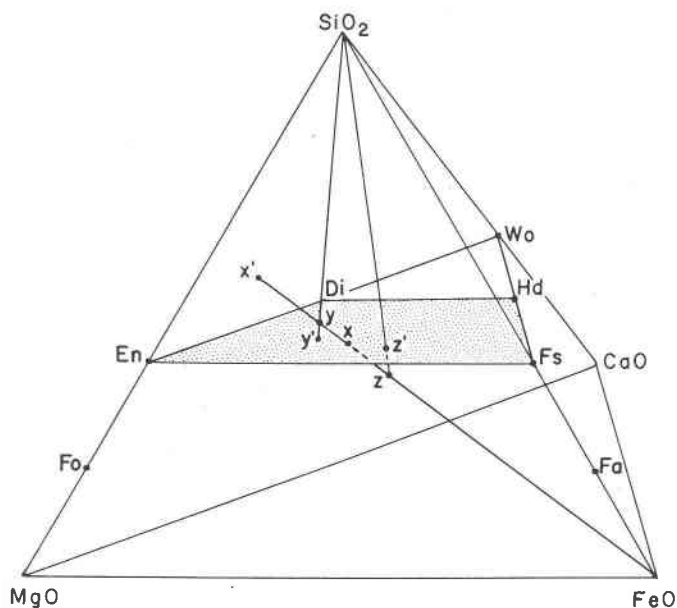


FIG. 1. Schematic diagram showing the pyroxene quadrilateral (shaded) in the more general system MgO-CaO-FeO-SiO₂. Point X represents a desired composition in the plane. See text for details.

PREVIOUS WORK

The previous work on the peripheral systems has been detailed by Yoder *et al.* (1963) and need not be repeated here. To the best of the author's knowledge, no other experimental work on synthetic mixtures falling within the pyroxene quadrilateral has been undertaken.¹

EXPERIMENTAL PROCEDURE

In general, the methods used were those described previously by the author (Roedder, 1952a). Details on the preparation of raw materials² and homogeneous glasses, temperature control and measurement, furnace design and operation, and analytical procedure are given in that paper and need not be repeated here. The nature of the system required some modification of the techniques used, however, as given below.

Batches of raw materials to make 10 grams of glass of the desired

¹ König (1960) studied a few mixtures, but only with added jadeite or aegirine.

² The source of the calcium used was a special high-purity precipitated CaCO₃, low in alkalis. Before weighing it was dried at 300° overnight. The source of the magnesium used was reagent-grade MgO, ignited at 1500° for one hour prior to use (Roedder, 1951).

composition were fused at about 1450° C. in pure iron crucibles, with pure iron chips, in a carefully purified nitrogen atmosphere. The quenched glass was separated from the iron chips, powdered, and re-fused with iron chips as often as necessary to achieve homogeneity. As is generally known, the *relative* concentrations of CaO, MgO, and SiO₂ in such glasses are fixed by synthesis, but the amounts of FeO in the final glasses will vary and cannot be controlled accurately even by careful synthesis procedures. Hence a portion of each homogeneous glass was held slightly above its liquidus temperature for an appropriate time, quenched, and then analyzed chemically for FeO and Fe₂O₃, using a modified Pratt method described earlier (Roedder, 1952a, p. 442-443). The amount of Fe₂O₃ varies directly with the total amount of iron in the batch, but it is also affected by the temperature of the fusion, and by the other constituents present. In the calculation and plotting of batch composition from the analyses, described below, all Fe₂O₃ was recalculated to the equivalent FeO ($\text{Fe}_2\text{O}_3 \times 0.8998 = \text{FeO}$). Although not strictly correct, this artifice was used as the simplification achieved was great, and the amount of Fe₂O₃ was small (1.36 per cent or less).

Each batch represents an attempt to synthesize a composition falling at a specific point in the pyroxene quadrilateral. In the general case this is never achieved. The actual major variable is FeO, but as the pyroxene quadrilateral is a plane at 50 mole per cent SiO₂ in the tetrahedron representing the more general system MgO-CaO-FeO-SiO₂ (Fig. 1), it is most convenient to express the nearness of approach of a composition to this plane in terms of deviation from 50 mole per cent SiO₂. In Fig. 1, composition X represents a desired composition lying in the pyroxene quadrilateral. In effect, the synthesis procedure is to add iron oxide to a mixture corresponding to the iron oxide-free equivalent point, X'. As the iron oxide in the final glass is the result of the interaction of the iron oxide actually added with the crucible walls and iron chips, the exact amount in the final glass is unknown until analyzed.

In general the glass, on analysis, will be found to have either *too little* FeO, and hence fall *above* the quadrilateral (Point Y), or will have *too much* FeO, and fall *below* the quadrilateral (Point Z). If, upon calculation, the distance Y-Y' (or Z-Z') corresponds to <0.5 mole per cent SiO₂, the batch was considered to be adequate for use and its position on the quadrilateral was plotted as projected point Y' (or Z'). Note was made, however, of the excess or deficiency of SiO₂ ("ΔSiO₂"), as indicated in Table 1. The variation in experimental conditions affecting the FeO content was such that most batches did not fall within the arbitrary limits of ±0.5 mole per cent SiO₂ upon analysis,¹ and the compositions

¹ Most batches fell within ±2 mole per cent SiO₂ of the pyroxene quadrilateral on first analysis.

TABLE 1. SUMMARY OF DATA

Batch	Recalculated mole %, by synthesis and analysis ¹			Δ SiO ₂ mole % ²	Fe ₂ O ₃ wt. % ²	<i>n</i> of glass ³	Liquidus determination ⁴
	En	Wo	Fs				
1-2	70.27	8.66	21.07	(-1.47)	0.45	Xlf.	Ol. liq. >1450°
1-3	69.64	5.61	24.75	+1.49	0.66	Xlq.	Ol. liq. >1405°
1-4	55.76	9.62	34.62	-0.16	0.38	~1.64	Ol. (?) liq. sl. >1405°
1-5	43.05	9.28	47.67	(-0.97)	0.73	1.645	—
1-6	38.05	5.78	56.17	+0.23	1.06	1.665	Trid. liq. >1405°; Py. in 1356 ± 48°
1-6a	32.52	9.35	58.12	(-2.23)	0.92	1.66	—
1-7	23.63	10.20	66.17	(-0.81)	0.81	~1.67	—
1-9	0	10.94	89.06	(-0.57)	0.97	1.78	—
2-1	66.19	16.31	17.50	-0.37	0.30	Xlq. Xlf.	Ol. liq. >1450°
2-2	54.75	15.75	29.50	-0.26	0.53	1.627	Ol. liq. >1405°
2-2a	59.44	17.09	23.47	-0.40	0.53	Xlq.	Ol. liq. >1405°
2-3	52.45	18.11	29.44	-0.49	0.49	~1.625	Ol. liq. sl. >1366°
2-4	43.52	18.77	37.71	(-1.17)	0.50	1.640	Py. liq. 1344 ± 20°
2-5	34.67	19.94	45.39	-0.36	0.59	~1.66	Py. liq. sl. >1323°
2-6	23.08	19.90	57.02	-0.40	0.48	1.667	Py. liq. 1240 ± 13°
2-7	12.07	20.81	67.12	(-0.72)	0.74	1.685	—
2-8	0	22.04	77.96	-0.02	0.54	Xlq.	—
3-1	57.93	24.98	17.09	-0.40	0.13	Sl. >1.615	Ol. liq. >1405°
3-2	53.94	27.92	18.14	+0.10	0.31	~1.63	Ol. liq. 1386 ± 20°
3-3	40.78	26.35	32.87	-0.69	0.28	1.638	Ol. liq. 1345 ± 20°
3-4	30.83	26.59	42.58	(-1.94)	0.45	1.658	Py. liq. 1263 ± 10°
3-5	19.71	25.56	54.73	(-2.70)	1.36	1.67	Py. liq. sl. >1227°
3-6	11.30	29.24	59.46	(-0.55)	0.90	1.678	Liq. <1185° (¼ hr.)
3-7	0	30.94	69.06	(-1.36)	1.32	1.698	—
4-1	50.01	34.52	15.47	(-2.03)	0.46	1.618	Py. (?) liq. sl. >1366°
4-2	38.64	33.32	28.04	(-3.56)	0.89	1.64	Py. liq. 1291 ± 17°
4-3	29.59	34.05	36.36	(-3.70)	0.53	1.647	Py. liq. 1247 ± 23°
4-4	(23.5)	(40.7)	(35.8)	n.a.	n.a.	~1.67	Py. liq. >1227°
4-5	10.57	36.48	52.94	(-3.39)	0.83	1.666	Py. liq. sl. >1185°
4-6	0	(43.0)	(57.0)	n.a.	n.a.	1.693	—
5-1	37.64	40.57	21.79	(-3.93)	0.28	1.632	Py. liq. 1291 ± 17°
5-2	29.74	42.76	27.50	(-3.27)	0.38	>1.640	Py. liq. >1274°
5-3	19.49	42.02	38.49	(-4.39)	0.79	1.653	Py. liq. 1240 ± 13°
5-4	10.74	46.29	42.97	(-2.68)	1.01	1.658	Py. liq. 1206 ± 21°

¹ Values in parentheses were obtained by synthesis alone. En=enstatite, MgSiO₃; Wo=wollastonite, CaSiO₃; Fs=ferrosilite, FeSiO₃.

² Values in parentheses are previous analyses of batches that have not been reanalyzed after the last correction. Presumably they now lie closer to the pyroxene quadrilateral. n.a.=not analyzed.

³ Xlf.="crystals in furnace," *i.e.*, liquidus temperature > batch fusion temperature. Xlq.=crystals formed on quenching.

⁴ Ol.=olivine; Py.=pyroxene; Trid.=tridymite; liq.=liquidus; sl.=slightly (*i.e.*, probably <10°). All temperatures in degrees Celsius.

had to be "corrected." If there was an excess of SiO₂ (*i.e.*, iron oxide deficiency, point Y) an empirically determined amount of additional iron oxide was mixed into the remaining portion of the glass and another fusion made. If there was a deficiency of SiO₂ (*i.e.*, iron oxide excess, point Z) appropriate amounts of SiO₂ were added and another fusion made. In each case, another analysis was made of the resulting glass, and additional corrections and fusions were made when necessary.

DATA OBTAINED

The 34 final compositions are listed in Table 1 with their calculated deviations from the pyroxene quadrilateral. Those compositions having deviations of >0.5 mole per cent SiO_2 are batches that were not carried through the entire batch preparation process.

The equilibrium quench runs, in miniature pure iron foil envelopes in a pure nitrogen atmosphere, were generally made with the homogeneous glass, but some of the compositions were also pre-crystallized. One-half hour to one hour was apparently adequate for equilibrium at the liquidus in these compositions. Those quench runs that serve to limit specific stable phase changes are summarized in Table 1. The uncertainty, given in degrees plus or minus, represents solely the temperature interval between significant quench runs. In those six compositions where the spacing of runs on either side of the liquidus was large, but the quantity of crystals in the subliquidus run was very small (and the liquidus slope was low), the liquidus is listed as "slightly above" the lower temperature run. The true liquidus temperature is believed to be less than 10 degrees above the temperature given for these six. These data were used to draw the tentative diagram for the liquidus surface in the system (Fig. 2).

No exact determinations of the solidus were made, but a number of the compositions in the pyroxene field showed very large amounts of crys-

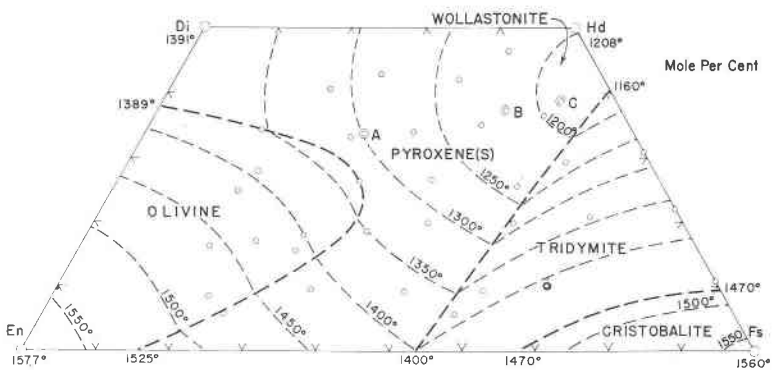


FIG. 2. Tentative phase diagram of the liquidus surface in the pyroxene system enstatite-diopside-hedenbergite-ferrosilite (En-Di-Hd-Fs). Circles represent compositions made; all runs on them were made in equilibrium with pure metallic iron and hence have the minimum amount of Fe_2O_3 . (See Table 1 and text.) The fields of olivine (solid solution) and of silica represent non-ternary equilibria. Temperatures in degrees Celsius. Points A, B, and C are four-phase points, representing equilibrium between liquid and: olivine + orthopyroxene + clinopyroxene (A); orthopyroxene + clinopyroxene + tridymite (B); and clinopyroxene + tridymite + wollastonite (C), taken from the "working diagram" of Yoder et al. (1963).

tallization and little or no glass in quench runs made about 100° below the liquidus. In the upper right-hand portion of the pyroxene field at < 30 mole per cent MgSiO_3 the solidus and liquidus are even closer, as compositions in these areas showed gross amounts of crystallization in the first 25° below the liquidus. This is to be expected from inspection of the available data on the limiting peripheral systems.

ACCURACY AND PRECISION OF THE DATA

There are many possible sources of the error in these data, and considerably more work would be needed to evaluate them individually. The presence of some ferric iron cannot be avoided. These melts were in equilibrium with their metallic iron containers, and hence the amount of ferric iron listed in Table 1 represents the minimum possible for each of these compositions. Certainly the amount of ferric iron will vary with the temperature, and hence most of the analyses were made on samples, several hundred milligrams in weight, held at slightly above the liquidus temperature for the same length of time as the quench runs used to determine the liquidus.

One important source of error lies in possible differences in composition between the quench run and the analyzed run. This may come about by local or general loss or gain of *ferrous* iron in the very small (10 mg) quench run samples heated in pure iron foil envelopes. Exceedingly minute amounts of organic dust¹—lint, paper, dandruff, etc.—will seriously affect the composition of iron-bearing glasses under these conditions. Similarly, almost invisible films of iron oxides inside the iron foil envelopes could cause serious local variations. For most of these runs, the foil envelopes were first prepared from annealed and carefully cleaned foil (Roedder, 1952a); they were then opened slightly to prevent internal adhesion and reannealed in pure nitrogen before use.

Almost all phase identification was based on petrographic measurements, as the small amount of crystals present in liquidus runs generally precludes the use of x-ray identification procedures. The crystals obtained were too small ($\sim 30\mu$) to show any distinctive color or pleochroism in transmitted light. The crystal habit and optical properties of the olivines obtained were approximately those reported by Bowen and Schairer (1935) for olivines in the system MgO-FeO-SiO_2 , and by Roedder (1951) in the system $\text{K}_2\text{O-MgO-SiO}_2$, but certainly some calcium is present in these crystals. The tridymite occurred as irregular or tabular crystals having the usual very low birefringence and refractive indices. No attempt was made to identify the various forms of MgSiO_3 , nor to

¹ A speck that is essentially invisible— 60μ —could reduce a significant portion of a quench run by as much as 1 weight per cent of FeO .

differentiate between the several forms of pyroxene within the quadrilateral, and it is not at all certain that the time used in the quenching runs would have been adequate to establish true equilibrium in these respects. As a consequence the field for "pyroxenes" in Fig. 2 includes orthopyroxenes, clinopyroxenes, and probably wollastonites. The data of Bowen *et al.* (1933) and Turnock (1962) indicate that there should be a field for wollastonite solid solution in the vicinity of the hedenbergite corner. Very little evidence is available to confirm the occurrence or extent of this field, but one run, on composition 5-4 at 1185°, showed a sufficiently large percentage of crystals that an *x*-ray identification could be attempted. The data obtained were not good, but were consistent with the presence of two phases, a hedenbergite-rich clinopyroxene, and a Ca-Fe wollastonite. A run made at 1185° on composition 4-5 was also checked by *x*-ray, although it contained a very small percentage of crystals. Only clinopyroxene was found, and wollastonite was not detected. A discussion of the probable inter-relationships of the several pyroxenes in this system is given by Yoder *et al.* (1963) and need not be repeated here; the boundary line across the pyroxene field in their diagram is indicated on Fig. 2 by the location of their points A, B, and C. The crystal habit of some of the pyroxene crystals formed at the liquidus permitted recognition of inclined extinction (along the upper, lime-rich part of the pyroxene field on Fig. 2), or of parallel extinction (along the lower, lime-poor part), in accord with the generally accepted fields for clinopyroxenes and orthopyroxenes. Unfortunately, most of the pyroxene crystals formed were subhedral or irregular, and their identification would require more extensive optical study.

There are several minor differences between the diagram presented here (Fig. 2) and the "working diagram" presented by Yoder *et al.* (1963), which was based on a variety of sources including the present author's work. In Fig. 2 the field for olivine does not extend as far toward the diopside-hedenbergite sideline as in the diagram of Yoder *et al.*, and the boundary between the fields of tridymite and pyroxene is straight rather than offset over to point B. The author's evidence for the positions of these two boundaries is not at all conclusive, and they were both drawn merely as the best fit to the limited experimental data available. The position of the high-lime part of the olivine boundary curve is based mainly on a few runs on composition 4-1. Although this composition was originally silica-deficient and was corrected, a second analysis was not made and the composition can only be assumed to lie closer to the pyroxene quadrilateral than the -2.03 mole per cent silica shown by the first analysis. The pyroxene liquidus determination of "slightly > 1366°" on this composition was based on a run at 1366° that showed a very few

large pyroxene crystals. For verification of this phase identification, however, a run made at 1323°, and containing perhaps as much as 50 per cent crystals, was *x*-rayed for possible olivine in addition to pyroxene. No olivine was found (*i.e.*, < 5 per cent of the sample). The boundary between the fields for pyroxene and silica was drawn as shown on Fig. 2, rather than up to point B and then over to the hedenbergite-ferrosilite join as shown by Yoder *et al.*, on the basis of runs on compositions 3-5 and 4-5. Unfortunately, neither of these compositions was analyzed after the last correction, but both showed a pyroxene liquidus, with no silica phase visible. It should be noted, however, that due to the geometry of the phase volumes for olivine solid solution and for tridymite in the tetrahedron representing the system MgO-CaO-FeO-SiO₂, the three-phase surfaces (two crystal phases plus liquid) for olivine plus pyroxene, and for pyroxene plus silica, both cross the pyroxene quadrilateral plane at low angles. Thus the apparent intersections with the quadrilateral—the boundary curves shown on Fig. 2—will be strongly influenced by rather minor deviations of the compositions studied from the actual pyroxene quadrilateral.

The author is indebted to P. Toulmin, 3rd, for the *x*-ray measurements and to P. Toulmin, 3rd, H. S. Yoder, Jr. and C. E. Tilley for manuscript review.

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- Manuscript received, August 13, 1964; accepted for publication, October 30, 1964.*