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ORTHO- AND CLINOPYROXENE COMPOSITIONS IN ORDINARY CHONDRITES AND RELATED BLANDER MODEL CALCULATION PROCEDURES

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1. Abstract

This report consists essentially of ortho- and clinopyroxene analyses that were used as a basis for a previous publication entitled "Restudy of the Pyroxene-Pyroxene Equilibration Temperatures for Ordinary Chondrite Meteorites" by Bunch and Olsen (1973). In addition, detailed procedures for calculation of the Ca effect on Fe^{2+}-Mg ion exchange equilibria in pyroxenes, using the Blander model (Blander, 1972), are presented.

2. Analytical Methods

We employed standard microprobe techniques for the analyses (15 kV, 0.03 μA, and 40 sec counting time). However, to ensure the most accurate data possible, we ran duplicate analyses on three grains each of opx and cpx (a few specimens contain less than three cpx grains) together with two different raw data correction methods as checks on analytical precision and correction procedures. Only those analytical summations of between 99.20 and 100.80 wt.%, and cation summations between 3.980 and 4.020 (based on 6 oxygens) were used. In addition, those clinopyroxenes with an FeO variation (among three grains) of >10% of the amounts present and >5% variation for MgO were discarded. Similarly, specimens showing variations of >15% for FeO and >8% MgO for orthopyroxene were also discarded.

3. Ortho- and Clinopyroxene Analyses

Analyses, structural formulae, and end-member compositions of most opx and cpx used in the initial study are given in Tables 1-6. In addition, data for pyroxenes in disequilibrated or nonequilibrated chondritic meteorites are given in Tables 7 and 8.

4. Additional Analytical Results

The amount of CaO in clinopyroxene (cpx) vs. CaO in orthopyroxene (opx) shows a dependence on classification (Fig. 1), with H-group cpx having the highest CaO content and LL-group cpx the lowest. On the other hand, opx shows an inverse relationship with LL-group opx having the highest CaO and H-group opx the lowest; the analytical scatter is quite large for opx, causing overlap among LL and L data points. Davis and Boyd (1966) have indicated that CaO in both pyroxenes is a function of temperature, although we have shown previously (Bunch and Olsen, 1973) and will show below, that all ordinary chondrites equilibrated at the same temperature, regardless of CaO content.

There has been some disagreement in the literature as to the actual existence of LL-group chondrites since Keil and Fredriksson (1964) proposed this classification. They demonstrated a distinct grouping of H, L, and LL chondrites using many compositional parameters. Ratios of Fe/(Fe + Mg) in olivine vs. Fe/(Fe + Mg) in cpx, for example, show a clear separation of the three groups. Similarly, mole percent Fe in cpx vs. mole percent Fe in opx analyzed in this work shows a clear separation of H, L, and LL pyroxenes (Fig. 2) and supports the argument for an LL-group of ordinary chondrites.

5. Blander Model Calculations for Ca Effect on Clino-Orthopyroxene Equilibria

Blander (1972) has placed serious doubt on the validity of the pyroxene-pyroxene geothermometer if the strong preference of Ca^{2+} ions for M(2) sites in cpx is considered. According to Blander, this strong preference of Ca for M(2) sites blocks these sites in cpx and the Fe^{2+}-Mg exchange equilibria is thus highly sensitive to Wo content. This effect on thermodynamic properties is calculated by three equilibria, which are partly dependent on three $\Delta G°$ values; two are known and the third ($\Delta G°_{13}$) is unknown, the best estimate of this value by Blander being -425 cal/mole. Now, to calculate the Ca effect on our H, L, and LL pyroxene equilibria, i.e., to calculate a curve to pass through the H, L, and LL group $(Fe/Mg)^{cpx}/(Fe/Mg)^{opx}$ with the appropriate Wo content using Blander's equations and constants, a temperature of ~1500° C is required, which probably indicates that Blander's estimate of $\Delta G°_{13}$ is wrong. By assuming an equilibration temperature for the H-group to be 800° C and then using Blander's equations, the calculations can be run in reverse to compute $\Delta G°_{13}$, which calculates to be +330 cal/mole.

After the necessary F-numbers (site fractions) are calculated for each of the three Wo contents, a set of calculated X_{Fe}^{cpx} values are obtained for each Wo value.

Next, we obtain

$$\frac{X_{Fe}^{cpx}}{X_{Mg}^{opx}} = \frac{X_{Fe}^{opx}}{1 - X_{Fe}^{opx}}$$

and then

$$\frac{X_{Fe}^{cpx}}{X_{Mg}^{opx}} = \frac{X_{Fe}^{cpx}}{1 - X_{Fe}^{cpx} - X_{Ca}^{cpx}} = \frac{X_{Fe}^{cpx}}{1 - X_{Fe}^{cpx} - Wo}$$

We now have values for the coexisting pyroxenes in terms of the ratios Kretz (1963) used, and these are plotted to construct curves that pass through our original group average $(Fe/Mg^{opx})/(Fe/Mg^{cpx})$ points, which means that the spread of observed points is completely accounted for by differences in Wo content and all chondrite groups equilibrated at the same temperature.

The following is the detailed procedure we followed for calculating the Ca effect on Fe-Mg exchange equilibria for H-, L-, and LL-group chondrite pyroxenes:

To Blander's reaction (11), p. 791, there is a ΔG°_{12}

To Blander's reaction (12), p. 792, there is a ΔG°_{13}

To Blander's reaction (13), p. 792, there is a ΔG°_{34}

Good estimates are given for ΔG°_{12} and ΔG°_{34};

ΔG°_{12} = 3600 cal/mole, ΔG°_{34} = 7500 cal/mole.

ΔG°_{13} was a rough guess at -425 cal/mole. By using this value in the equation, a temperature of 1500° C would be necessary to pass a curve through the H-group point in Fig. 3. Since this temperature is above the liquidus, it follows that the ΔG°_{13} value is in error, as we stated above. Therefore, we assumed an equilibrium temperature of 800° C, which allowed an estimate of +300 cal/mole to be made.

Since

$$\Delta G^\circ = -RT \ln K$$

then for 800° C

$$\Delta G^\circ_{12} = 3600, \ K_{12} = 0.1847;$$
$$\Delta G^\circ_{13} = 330, \ K_{13} = 0.8562;$$

and

$$\Delta G^\circ_{34} = 7500, \ K_{34} = 0.02966$$

To obtain Blander's F-numbers and to calculate distribution curves, we arbitrarily chose a set of F-numbers (which are convenient, independent variables in terms of the equation). We chose the F's to be 0.04, 0.12, and 0.20 in Table 9. For the H-group, Wo = 0.46 and the temperature is arbitrarily set at 800° C; all other variables are now fixed.

Example: for $F_1 = 0.04$; from Blander's equation (15a) (p. 792) we can calculate F_2 since

$$F_2 = \frac{F_1}{K_{12} + (1 - K_{12})}$$

where

$F_1 = 0.04$

$K_{12} = 0.1847$

Similarly, for $F_1 = 0.12$ and $F_1 = 0.20$, using the same K_{12} each time. The F_2's are given in Table 9. Now, $X_{Fe}^{opx} = \frac{F_1 + F_2}{2}$ (Blander's equation 16). From the chosen F_1 and calculated F_2, we get each X_{Fe}^{opx} as given in Table 9.

From Blander's equation (15b), we see that F_3 is a function of F_1 and K_{13}, which = 0.8562. Thus, we calculate that F_3's associated with each chosen F_1. These are listed in Table 9.

From Blander's equation (15c), we see that F_4 is a function of F_3, which we know is 0.02966. Thus, we obtain the F_4's associated with the original F_1's and the associated F_2's and F_3's.

Now, from Blander's equation (17), we see that

$$X_{Fe}^{cpx} = \frac{F_3}{2} + \left(\frac{1}{2} - W_o\right) F_4.$$

Since we have the calculated F_3's and F_4's, then for our chosen W_o content, 0.46, we get a set of calculated X_{Fe}^{cpx}.

Now, we obtain

$$\frac{X_{Fe}^{opx}}{X_{Mg}^{opx}}$$

which is

$$\frac{X_{Fe}^{opx}}{1 - X_{Fe}^{opx}}$$

and

$$\frac{X_{Fe}^{cpx}}{X_{Mg}^{cpx}}$$

which is

$$\frac{X_{Fe}^{cpx}}{1 - X_{Fe}^{cpx} - X_{Ca}^{cpx}} = \frac{X_{Fe}^{cpx}}{1 - X_{Fe}^{cpx} - W_o} = \frac{X_{Fe}^{cpx}}{1 - X_{Fe}^{cpx} - 0.46}$$

We now have values for the coexisting pyroxenes in terms of the ratios Kretz used, and these are ready for plotting. The next step is to repeat the entire process for the same F_1's (0.04, 0.12, 0.20) for each different Wo content (L = 0.45 and LL = 0.44). All K's remain the same. A summary of values is given in Table 9. Data points from these calculations are plotted in Fig. 3 and curves are drawn through these points, which pass through the group averages for H, L, and LL pyroxenes. This means, of course, that the spread in the observed points is completely accounted for by the difference in Wo content--they represent the same temperature. The value of 800° C is not significant, since it was chosen to calculate a reasonable ΔG_{13}° value. Any arbitrarily chosen temperature and resulting ΔG_{13}° value would produce curves that plot in exactly the same place. Until we know an experimentally or empirically determined temperature, with well-determined ratios XFe/XMg for each pyroxene and very accurate Wo contents, the pyroxene-pyroxene geothermometry is useful only as an indicator of relative temperatures.

References

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Table 1. H6 Orthopyroxenes

	Oakley 1	Oakley 2	Oakley 3	Estacado 1	Estacado 2	Estacado 3	Guareña 1	Guareña 2	Guareña 3	Cedar 1	Cedar 2	Cedar 3	Cape Giradeau 1	Cape Giradeau 2	Cape Giradeau 3	Kernouve 1	Kernouve 2	Kernouve 3
SiO_2	55.3	56.2	56.3	55.7	55.8	55.0	56.1	56.1	55.8	56.15	56.1	56.2	56.4	55.9	55.8	55.8	55.9	55.9
Al_2O_3	0.20	0.17	0.15	0.08	0.09	0.06	0.16	0.16	0.17	0.14	0.15	0.15	0.03	0.09	0.11	0.07	0.09	0.09
TiO_2	0.20	0.21	0.20	0.18	0.18	0.16	0.20	0.21	0.22	0.20	0.20	0.20	0.13	0.17	0.19	0.19	0.17	0.18
Cr_2O_3	0.09	0.10	0.13	0.10	0.11	0.06	0.12	0.10	0.10	0.11	0.09	0.12	0.08	0.11	0.09	0.10	0.10	0.10
FeO	12.3	11.6	11.6	11.2	10.7	11.2	10.9	11.2	11.5	11.2	11.2	11.2	11.4	11.7	11.2	10.9	10.7	10.8
MnO	0.48	0.50	0.36	0.56	0.55	0.56	0.50	0.52	0.50	0.47	0.46	0.47	0.53	0.52	0.51	0.51	0.57	0.57
MgO	30.35	30.1	30.1	31.3	31.3	31.7	30.6	30.8	30.8	30.5	30.85	30.7	31.4	31.2	31.1	31.4	31.3	31.3
CaO	0.43	0.67	0.58	0.42	0.67	0.49	0.79	0.62	0.69	0.68	0.39	0.67	0.49	0.82	0.80	0.57	0.55	0.55
Total	99.35	99.55	99.42	99.54	99.40	99.23	99.37	99.71	99.78	99.45	99.44	99.71	100.46	100.51	99.80	99.54	99.38	99.49
	OXYGEN ON BASIS OF 6(O)																	
Si	1.966	1.997	2.001	1.979	1.982	1.964	2.000	2.000	1.969	1.994	1.992	1.991	1.985	1.974	1.979	1.980	1.985	1.984
Al	0.008	0.007	0.006	0.003	0.004	0.003	0.007	0.007	0.007	0.006	0.006	0.006	0.001	0.004	0.005	0.003	0.004	0.004
Ti	0.005	0.006	0.005	0.005	0.005	0.004	0.005	0.006	0.006	0.005	0.005	0.005	0.003	0.005	0.005	0.005	0.005	0.005
Cr	0.002	0.003	0.003	0.003	0.003	0.001	0.003	0.003	0.003	0.003	0.002	0.003	0.002	0.003	0.002	0.003	0.003	0.003
Fe	0.401	0.345	0.345	0.333	0.318	0.335	0.328	0.336	0.346	0.333	0.333	0.332	0.336	0.346	0.332	0.323	0.318	0.321
Mn	0.015	0.015	0.011	0.017	0.017	0.017	0.015	0.016	0.015	0.014	0.014	0.014	0.016	0.016	0.015	0.017	0.017	0.017
Mg	1.609	1.594	1.595	1.658	1.657	1.687	1.640	1.647	1.649	1.615	1.632	1.621	1.648	1.642	1.644	1.660	1.656	1.655
Ca	0.016	0.026	0.022	0.016	0.026	0.019	0.030	0.024	0.027	0.026	0.015	0.025	0.019	0.031	0.030	0.021	0.021	0.021
Σ	4.023	3.992	3.989	4.013	4.010	4.030	4.009	4.020	4.021	3.997	3.999	3.999	4.010	4.019	4.013	4.013	4.008	4.009
Fs	18.0	17.5	17.6	16.6	15.9	16.4	16.4	16.7	17.1	16.9	16.8	16.8	16.8	17.1	16.6	16.1	15.9	16.1
En	81.0	81.2	81.3	82.6	82.8	82.7	82.1	82.1	81.6	81.8	82.5	81.9	82.3	81.4	81.9	82.8	83.0	82.9
Wo	1.0	1.3	1.1	0.80	1.3	0.90	1.5	1.2	1.3	1.3	0.70	1.3	0.90	1.5	1.50	1.10	1.1	1.0

Table 2. L6 Orthopyroxenes

	Mocs 2	Mocs 3	Colby 1	Colby 2	Colby 3	Langhalsen 1	Langhalsen 2	Langhalsen 3	Kyushu 1	Kyushu 2	Kyushu 3	Bath Furnace 3	Bruderheim 1	Bruderheim 2	Bruderheim 3	Modoc 1	Modoc 2	Modoc 3
SiO_2	55.4	55.9	56.1	56.5	56.7	56.2	55.7	55.6	55.7	56.3	55.9	55.5	54.8	54.8	54.6	55.5	55.6	55.4
Al_2O_3	0.18	0.15	0.02	0.05	0.06	0.15	0.15	0.14	0.17	0.16	0.16	0.14	0.12	0.12	0.09	0.14	0.13	0.13
TiO_2	0.21	0.21	0.17	0.14	0.17	0.21	0.22	0.20	0.21	0.20	0.23	0.21	0.21	0.21	0.17	0.17	0.20	0.21
Cr_2O_3	0.19	0.11	0.07	0.07	0.07	0.09	0.09	0.10	0.19	0.11	0.12	0.18	0.11	0.10	0.08	0.09	0.08	0.10
FeO	14.0	13.7	13.5	13.5	13.2	14.1	13.9	14.0	14.1	14.0	13.9	14.2	13.3	13.3	13.8	13.8	13.6	13.7
MnO	0.45	0.46	0.49	0.48	0.51	0.45	0.44	0.45	0.47	0.47	0.49	0.46	0.48	0.48	0.47	0.46	0.44	0.45
MgO	28.7	28.9	29.3	28.8	29.0	28.75	28.6	28.6	28.4	28.4	28.0	28.2	29.5	29.55	29.5	28.6	28.8	28.6
CaO	0.79	0.82	0.61	0.70	0.60	0.56	0.59	0.55	0.68	0.87	0.64	0.77	0.61	0.73	0.61	0.64	0.54	0.64
Total	99.92	100.25	100.26	100.24	100.31	100.51	99.69	99.64	99.83	100.51	99.44	99.66	99.13	99.29	99.32	99.40	99.39	99.23
OXYGEN ON BASIS OF 6(O)																		
Si	1.986	1.993	1.997	2.009	2.011	1.999	1.997	1.996	1.997	2.003	1.996	1.996	1.976	1.973	1.970	1.995	1.989	1.991
Al	0.008	0.006	0.001	0.002	0.003	0.006	0.006	0.006	0.007	0.007	0.007	0.006	0.005	0.005	0.004	0.006	0.006	0.006
Ti	0.006	0.006	0.005	0.004	0.005	0.006	0.006	0.005	0.006	0.005	0.006	0.006	0.006	0.006	0.005	0.006	0.005	0.006
Cr	0.005	0.003	0.002	0.002	0.002	0.002	0.002	0.003	0.003	0.003	0.003	0.005	0.003	0.003	0.002	0.002	0.002	0.003
Fe	0.420	0.409	0.402	0.401	0.392	0.419	0.417	0.420	0.423	0.417	0.423	0.427	0.401	0.401	0.417	0.415	0.411	0.414
Mn	0.014	0.014	0.015	0.015	0.015	0.014	0.013	0.014	0.014	0.014	0.015	0.014	0.015	0.015	0.014	0.014	0.014	0.014
Mg	1.534	1.536	1.554	1.526	1.533	1.524	1.528	1.530	1.518	1.506	1.517	1.511	1.586	1.586	1.587	1.532	1.553	1.541
Ca	0.030	0.031	0.023	0.027	0.023	0.021	0.023	0.021	0.026	0.033	0.025	0.030	0.024	0.028	0.024	0.025	0.021	0.025
Σ	4.002	3.997	3.998	3.985	3.982	3.991	3.993	3.995	3.993	3.987	3.993	3.994	4.014	4.017	4.022	3.996	4.002	4.000
Fs	21.2	20.7	20.3	20.5	20.1	21.3	21.2	21.3	21.5	21.3	21.5	21.7	20.0	19.9	20.5	21.0	20.7	20.9
En	77.3	77.7	78.5	78.1	78.7	77.6	77.7	77.6	77.2	77.0	77.2	76.8	78.9	78.7	78.3	77.7	78.2	77.8
Wo	1.5	1.6	1.2	1.4	1.2	1.1	1.1	1.1	1.3	1.7	1.3	1.5	1.1	1.4	1.2	1.3	1.1	1.3

Table 3. LL6 Orthopyroxenes

	Lake Labyrinth 2	Lake Labyrinth 3	Dhurmsala 2	Dhurmsala 3	Nås 1	Nås 2	Nås 3	Ottawa 1	Ottawa 2	Ottawa 3	Manbhoom 1	Manbhoom 2	Manbhoom 3	Ensisheim 1	Ensisheim 2	Ensisheim 3
SiO_2	54.9	55.4	55.5	54.4	55.35	55.1	55.3	55.7	55.3	55.5	54.9	55.1	55.2	55.5	55.1	54.9
Al_2O_3	0.23	0.15	0.25	0.25	0.16	0.16	0.16	0.09	0.10	0.07	0.15	0.15	0.17	0.15	0.16	0.13
TiO_2	0.21	0.21	0.28	0.28	0.20	0.23	0.20	0.18	0.18	0.18	0.21	0.21	0.19	0.21	0.21	0.19
Cr_2O_3	0.13	0.15	0.34	0.34	0.09	0.10	0.11	0.16	0.12	0.12	0.11	0.11	0.12	0.10	0.11	0.09
FeO	16.7	15.7	15.0	15.0	17.1	16.5	16.4	16.2	16.3	16.5	16.4	16.7	16.4	15.5	15.6	15.9
MnO	0.42	0.42	0.47	0.47	0.44	0.43	0.42	0.47	0.45	0.46	0.42	0.41	0.41	0.48	0.46	0.47
MgO	26.8	26.7	28.0	27.7	27.0	26.6	26.75	27.2	27.1	27.0	26.7	26.8	26.9	27.5	27.0	26.9
CaO	0.89	1.32	0.90	0.89	0.66	0.77	0.91	0.82	1.02	0.99	0.84	0.77	0.75	0.68	0.71	0.64
Total	100.28	100.05	100.74	99.33	101.00	99.89	100.25	100.82	100.57	100.82	99.73	100.25	100.14	100.12	99.35	99.22

OXYGEN ON BASIS OF 6(O)

	Lake Labyrinth 2	Lake Labyrinth 3	Dhurmsala 2	Dhurmsala 3	Nås 1	Nås 2	Nås 3	Ottawa 1	Ottawa 2	Ottawa 3	Manbhoom 1	Manbhoom 2	Manbhoom 3	Ensisheim 1	Ensisheim 2	Ensisheim 3
Si	1.986	2.000	1.984	1.976	1.989	1.997	1.996	1.997	1.991	1.994	1.993	1.992	1.994	1.997	1.999	1.998
Al	0.010	0.006	0.011	0.011	0.007	0.007	0.007	0.004	0.004	0.003	0.006	0.006	0.007	0.006	0.007	0.006
Ti	0.006	0.006	0.008	0.008	0.005	0.006	0.005	0.005	0.005	0.005	0.006	0.006	0.005	0.006	0.006	0.005
Cr	0.003	0.004	0.009	0.009	0.002	0.003	0.003	0.004	0.003	0.003	0.003	0.003	0.003	0.003	0.003	0.002
Fe	0.505	0.474	0.448	0.456	0.514	0.500	0.495	0.486	0.491	0.496	0.498	0.505	0.495	0.466	0.473	0.484
Mn	0.013	0.013	0.014	0.015	0.013	0.013	0.013	0.014	0.014	0.014	0.013	0.013	0.013	0.015	0.014	0.015
Mg	1.445	1.436	1.492	1.500	1.446	1.437	1.439	1.453	1.454	1.446	1.445	1.444	1.448	1.475	1.460	1.459
Ca	0.085	0.051	0.035	0.035	0.025	0.030	0.035	0.032	0.039	0.038	0.033	0.030	0.030	0.026	0.028	0.025
Σ	4.002	3.990	3.999	4.007	4.002	3.992	3.994	3.994	4.001	3.998	3.997	3.998	3.997	3.993	3.990	3.993
Fs	25.5	24.2	22.7	22.9	25.9	25.4	25.1	24.6	24.7	25.1	25.2	25.5	25.1	23.7	24.1	24.6
En	72.8	73.2	75.5	75.4	72.8	73.1	73.1	73.8	73.3	73.0	73.1	73.0	73.4	75.0	74.5	74.1
Wo	1.7	2.6	1.8	1.7	1.3	1.5	1.8	1.6	2.0	1.9	1.7	1.5	1.5	1.3	1.4	1.3

Table 4. H6 Clinopyroxenes

	Oakley 1	Oakley 2	Oakley 3	Estacado 1	Estacado 2	Estacado 3	Guareña 1	Guareña 2	Guareña 3	Cedar 1	Cedar 2	Cedar 3	Cape Giradeau 1	Cape Giradeau 2	Cape Giradeau 3	Kernouve 2	Kernouve 3
SiO_2	54.4	54.65	54.6	54.5	54.0	54.1	53.8	54.0	54.0	54.4	54.8	54.4	54.4	54.4	54.4	54.0	53.6
Al_2O_3	0.44	0.64	0.46	0.58	0.50	0.70	0.39	0.47	0.39	0.48	0.41	0.46	0.51	0.51	0.46	0.52	0.49
TiO_2	0.47	0.47	0.47	0.50	0.45	0.46	0.51	0.48	0.48	0.43	0.43	0.47	0.43	0.50	0.51	0.48	0.47
Cr_2O_3	0.56	0.56	0.55	0.57	0.54	0.53	0.57	0.61	0.62	0.55	0.52	0.62	0.69	0.68	0.65	0.64	0.65
FeO	3.86	3.75	3.69	3.44	3.46	3.83	3.76	3.65	4.16	3.56	3.60	4.24	4.70	4.80	4.80	3.68	4.36
MnO	0.22	0.24	0.23	0.26	0.29	0.26	0.22	0.22	0.24	0.21	0.20	0.23	0.25	0.25	0.22	0.30	0.31
MgO	16.8	16.8	17.8	16.7	16.85	16.4	16.9	16.9	17.0	16.4	16.2	16.3	17.5	17.1	17.2	17.1	16.8
CaO	22.3	22.7	21.3	22.6	22.7	22.4	23.0	22.7	22.9	22.8	22.8	22.1	21.7	22.2	21.9	22.5	22.3
Na_2O	0.45	0.45	0.42	0.55	0.48	0.48	0.41	0.42	0.46	0.44	0.41	0.46	0.60	0.49	0.50	0.49	0.51
Total	99.50	100.26	99.52	99.70	99.27	99.16	99.56	99.45	100.25	99.27	99.37	99.28	100.78	100.93	100.64	99.71	99.49
	OXYGEN ON BASIS OF 6(O)																
Si	1.994	1.989	1.993	1.993	1.986	1.991	1.978	1.984	1.975	1.997	2.009	2.001	1.977	1.976	1.980	1.979	1.976
Al	0.019	0.028	0.020	0.025	0.022	0.030	0.017	0.020	0.017	0.021	0.018	0.020	0.022	0.022	0.020	0.023	0.021
Ti	0.013	0.013	0.013	0.014	0.012	0.013	0.014	0.013	0.013	0.012	0.012	0.013	0.012	0.014	0.014	0.013	0.013
Cr	0.015	0.014	0.014	0.015	0.014	0.014	0.015	0.016	0.016	0.014	0.013	0.016	0.018	0.018	0.017	0.017	0.017
Fe	0.118	0.114	0.113	0.105	0.106	0.118	0.116	0.112	0.127	0.110	0.110	0.130	0.143	0.146	0.146	0.113	0.134
Mn	0.007	0.007	0.007	0.009	0.009	0.008	0.007	0.007	0.007	0.007	0.006	0.007	0.008	0.008	0.007	0.009	0.010
Mg	0.918	0.911	0.969	0.910	0.924	0.900	0.926	0.925	0.927	0.899	0.885	0.894	0.948	0.926	0.933	0.934	0.923
Ca	0.876	0.885	0.833	0.885	0.894	0.883	0.906	0.893	0.897	0.899	0.896	0.871	0.845	0.864	0.854	0.884	0.880
Na	0.032	0.032	0.030	0.039	0.034	0.034	0.029	0.030	0.033	0.031	0.029	0.033	0.042	0.035	0.035	0.035	0.036
Σ	3.992	3.993	3.992	3.993	4.001	3.991	4.007	4.000	4.012	3.989	3.978	3.985	4.013	4.008	4.006	4.006	4.011
Fs	6.2	6.0	5.9	5.5	5.5	6.2	5.9	5.8	6.5	5.7	5.8	6.9	7.4	7.5	7.6	5.8	6.9
En	48.0	47.7	50.6	47.9	48.0	47.3	47.5	47.9	47.5	47.2	46.8	47.1	49.0	47.8	48.2	48.4	47.6
Wo	45.9	46.3	43.5	46.6	46.5	46.5	46.5	46.3	46.0	47.1	47.4	46.0	43.6	44.6	44.2	45.8	45.5

Table 5. L6 Clinopyroxenes

	Mocs 3	Colby 1	Colby 2	Colby 3	Kyushu 1	Kyushu 2	Langhalsen 1	Langhalsen 2	Langhalsen 3	Bath Furnace 1	Bath Furnace 2	Bruderheim 1	Bruderheim 2	Bruderheim 3	Modoc 1	Modoc 3
SiO_2	54.0	54.9	54.6	54.8	53.9	53.8	53.9	54.0	54.2	54.0	53.8	54.3	54.3	54.2	54.6	54.4
Al_2O_3	0.50	0.34	0.48	0.34	0.45	0.43	0.45	0.50	0.47	0.35	0.45	0.46	0.43	0.45	0.46	0.44
TiO_2	0.47	0.40	0.44	0.38	0.48	0.43	0.43	0.45	0.48	0.37	0.41	0.44	0.43	0.45	0.46	0.47
Cr_2O_3	0.64	0.55	0.63	0.53	0.62	0.62	0.62	0.61	0.61	0.11	0.53	0.65	0.59	0.65	0.66	0.69
FeO	5.20	5.1	4.7	4.7	5.2	5.5	4.8	4.95	4.9	5.9	5.7	5.3	4.7	5.5	5.2	5.3
MnO	0.21	0.22	0.22	0.22	0.24	0.25	0.20	0.20	0.20	0.39	0.20	0.25	0.22	0.24	0.21	0.22
MgO	16.15	16.4	16.5	16.5	16.6	16.6	16.2	16.4	16.2	16.4	16.4	16.3	16.1	16.1	15.6	15.7
CaO	22.1	22.6	22.2	22.0	21.6	21.4	21.8	21.6	21.7	21.6	21.6	21.8	22.0	21.3	21.5	21.5
Na_2O	0.58	0.40	1.11	0.43	0.51	0.51	0.57	0.62	0.60	0.08	0.53	0.52	0.45	0.50	0.49	0.49
Total	99.85	100.91	100.88	99.90	99.60	99.54	98.97	99.33	99.36	99.20	99.62	100.02	99.22	99.39	99.18	99.21
							OXYGEN ON BASIS OF 6(O)									
Si	1.986	1.995	1.986	2.005	1.985	1.985	1.995	1.991	1.997	1.994	1.985	1.992	1.998	1.999	2.006	2.008
Al	0.022	0.015	0.021	0.015	0.020	0.019	0.020	0.022	0.020	0.015	0.020	0.020	0.019	0.020	0.020	0.019
Ti	0.013	0.011	0.012	0.011	0.013	0.012	0.012	0.013	0.013	0.010	0.011	0.012	0.012	0.013	0.013	0.013
Cr	0.017	0.014	0.016	0.014	0.016	0.016	0.016	0.016	0.016	0.003	0.014	0.017	0.016	0.017	0.017	0.018
Fe	0.160	0.155	0.143	0.144	0.160	0.170	0.149	0.153	0.151	0.183	0.176	0.163	0.145	0.170	0.162	0.162
Mn	0.007	0.007	0.007	0.007	0.008	0.008	0.006	0.006	0.006	0.012	0.006	0.008	0.007	0.008	0.007	0.007
Mg	0.886	0.889	0.895	0.900	0.911	0.913	0.894	0.902	0.890	0.908	0.902	0.891	0.888	0.885	0.864	0.864
Ca	0.871	0.880	0.865	0.862	0.852	0.846	0.864	0.854	0.857	0.859	0.854	0.857	0.872	0.842	0.856	0.851
Na	0.041	0.028	0.078	0.031	0.036	0.037	0.041	0.044	0.043	0.006	0.038	0.037	0.032	0.036	0.035	0.035
$\sum$	4.002	3.994	4.023	3.986	4.002	4.004	3.996	4.000	3.993	3.990	4.006	3.996	3.989	3.988	3.980	3.978
Fs	8.3	8.0	7.5	7.5	8.3	8.8	7.8	8.0	8.0	9.4	9.1	8.5	7.6	8.9	8.6	8.7
En	46.2	46.2	47.0	47.2	47.4	47.3	46.9	47.3	46.9	46.5	46.7	46.7	46.6	46.7	45.9	46.0
Wo	45.5	45.8	45.5	45.3	44.3	43.9	45.3	44.7	45.1	44.1	44.2	44.8	45.8	44.4	45.5	45.3

Table 6. LL6 Clinopyroxenes

	Lake Labyrinth 1	Lake Labyrinth 2	Dhurmsala 1	Dhurmsala 2	Dhurmsala 3	Näs 1	Näs 2	Ottawa 1	Ottawa 2	Ottawa 3	Manbhoom 2	Manbhoom 3	Ensisheim 1	Ensisheim 2	Ensisheim 3
SiO_2	53.3	53.8	53.9	53.8	54.7	54.1	53.6	53.6	53.5	53.3	54.2	54.2	53.05	53.45	53.4
Al_2O_3	0.44	0.42	0.42	0.40	0.43	0.47	0.46	0.45	0.43	0.43	0.40	0.42	0.35	0.33	0.40
TiO_2	0.45	0.46	0.43	0.44	0.42	0.46	0.45	0.46	0.46	0.45	0.42	0.42	0.46	0.39	0.47
Cr_2O_3	0.59	0.63	0.58	0.55	0.44	0.60	0.62	0.66	0.68	0.65	0.63	0.65	0.57	0.56	0.66
FeO	7.15	6.4	5.4	6.1	5.6	6.5	6.6	7.1	6.4	6.4	6.5	6.6	6.3	6.6	7.2
MnO	0.20	0.22	0.22	0.24	0.28	0.21	0.20	0.25	0.25	0.34	0.21	0.20	0.21	0.22	0.24
MgO	15.7	16.0	16.2	16.4	15.9	15.5	15.4	16.3	16.3	16.4	15.2	15.2	16.0	16.3	16.2
CaO	21.5	21.7	21.7	21.6	21.1	21.5	21.5	21.2	21.1	20.8	21.0	21.0	21.8	21.2	21.25
Na_2O	0.47	0.52	0.44	0.43	0.30	0.56	0.55	0.49	0.48	0.47	0.48	0.44	0.40	0.38	0.43
Total	99.80	100.15	99.29	99.96	99.17	99.90	99.38	100.51	99.60	99.24	99.04	99.13	99.14	99.43	100.25
							OXYGEN OF BASIS OF 6(O)								
Si	1.977	1.982	1.992	1.982	2.016	1.996	1.991	1.973	1.980	1.978	2.012	2.011	1.976	1.983	1.972
Aℓ	0.019	0.018	0.018	0.017	0.019	0.020	0.020	0.020	0.019	0.019	0.018	0.018	0.015	0.014	0.017
Ti	0.013	0.013	0.012	0.012	0.012	0.013	0.013	0.013	0.013	0.013	0.012	0.012	0.013	0.011	0.013
Cr	0.016	0.016	0.015	0.014	0.012	0.016	0.016	0.017	0.018	0.017	0.016	0.017	0.015	0.015	0.017
Fe	0.222	0.197	0.167	0.188	0.173	0.201	0.205	0.219	0.198	0.199	0.202	0.205	0.196	0.205	0.222
Mn	0.006	0.007	0.007	0.008	0.009	0.007	0.006	0.008	0.008	0.011	0.007	0.006	0.007	0.007	0.008
Mg	0.868	0.879	0.893	0.901	0.874	0.852	0.853	0.894	0.899	0.909	0.841	0.841	0.889	0.901	0.892
Ca	0.855	0.857	0.859	0.853	0.833	0.850	0.856	0.836	0.837	0.829	0.835	0.835	0.870	0.843	0.841
Na	0.034	0.037	0.032	0.031	0.021	0.040	0.040	0.035	0.034	0.033	0.035	0.032	0.029	0.027	0.031
Σ	4.010	4.006	3.995	4.005	3.968	3.994	3.998	4.014	4.010	4.010	3.977	3.976	4.010	4.010	4.013
Fs	11.4	10.2	8.7	9.7	9.2	10.5	10.7	11.2	10.2	10.3	10.7	10.9	10.0	10.5	11.4
En	44.6	45.5	46.5	46.4	46.5	44.8	44.6	45.9	46.5	46.9	44.8	44.7	45.5	46.3	45.6
Wo	44.0	44.3	44.8	43.9	44.3	44.7	44.7	42.9	43.2	42.8	44.5	44.4	44.5	43.2	43.0

Table 7. Non- or disequilibrated orthopyroxenes

	Shaw 1	Shaw 2	Shaw 3	Jelica 1	Jelica 2	Jelica 3	Leedey 1	Leedey 2	Bjurbole 1	Bjurbole 2	Bjurbole 3	Mt. Browne 1	Mt. Browne 2	Mt. Browne 3	Breamers 2	Cavour 2	Olivenza 1	Olivenza 2	Plainsco 4	Plainsco 5	Plainsco 6
SiO_2	55.1	55.8	54.6	54.9	54.8	54.6	55.6	54.8	56.6	56.5	56.7	55.9	56.2	55.5	55.5	55.7	55.9	54.9	54.8	54.9	54.7
Al_2O_3	0.56	0.28	0.29	0.22	0.15	0.17	0.13	0.22	0.06	0.05	0.18	0.02	0.05	0.0	0.17	0.13	0.16	0.11	0.17	0.18	0.16
TiO_2	0.17	0.09	0.09	0.23	0.18	0.19	0.18	0.20	0.10	0.10	0.14	0.08	0.09	0.14	0.22	0.22	0.21	0.18	0.18	0.18	0.20
Cr_2O_3	0.49	0.41	0.55	0.13	0.10	0.09	0.08	0.09	0.12	0.13	0.13	0.11	0.12	0.05	0.09	0.11	0.12	0.09	0.08	0.08	0.11
FeO	12.4	12.15	12.8	15.2	16.3	16.2	13.85	14.8	14.4	14.4	14.2	11.1	11.6	11.6	11.6	11.7	15.9	16.4	11.0	11.2	11.1
MnO	0.45	0.43	0.49	0.44	0.43	0.43	0.44	0.43	0.44	0.44	0.42	0.50	0.47	0.48	0.49	0.50	0.45	0.45	0.46	0.47	0.47
MgO	28.5	29.7	28.5	27.7	27.1	27.0	28.4	27.9	28.9	28.9	28.9	31.2	31.5	31.3	31.0	31.3	26.5	26.1	32.3	32.3	32.9
CaO	1.98	1.21	1.94	0.67	0.78	0.63	0.49	0.59	0.27	0.22	0.31	0.73	0.67	0.74	0.73	0.71	0.59	0.87	0.40	0.46	0.39
Total	99.65	100.07	99.26	99.49	99.84	99.31	99.17	99.03	100.89	100.74	100.98	99.64	100.70	99.81	99.80	100.37	99.83	99.10	99.39	99.77	100.03
	OXYGEN ON BASIS OF 6(O)																				
Si	1.976	1.984	1.972	1.987	1.987	1.989	2.000	1.989	2.005	2.005	2.005	1.984	1.980	1.973	1.972	1.969	2.016	2.006	1.952	1.951	1.939
Al	0.024	0.012	0.012	0.009	0.006	0.007	0.006	0.009	0.003	0.002	0.008	0.001	0.002	0.0	0.007	0.005	0.007	0.005	0.007	0.008	0.007
Ti	0.005	0.002	0.002	0.006	0.005	0.005	0.005	0.006	0.003	0.003	0.004	0.002	0.002	0.004	0.006	0.006	0.006	0.005	0.005	0.005	0.005
Cr	0.013	0.010	0.014	0.003	0.003	0.002	0.002	0.002	0.003	0.003	0.003	0.003	0.003	0.001	0.002	0.003	0.003	0.002	0.002	0.002	0.003
Fe	0.372	0.361	0.387	0.460	0.494	0.494	0.418	0.449	0.427	0.427	0.420	0.329	0.341	0.345	0.345	0.346	0.480	0.501	0.328	0.333	0.329
Mn	0.014	0.013	0.015	0.014	0.013	0.013	0.014	0.013	0.013	0.013	0.013	0.015	0.014	0.015	0.015	0.015	0.014	0.014	0.014	0.014	0.014
Mg	1.523	1.574	1.534	1.494	1.464	1.466	1.528	1.509	1.526	1.528	1.523	1.650	1.652	1.658	1.642	1.650	1.425	1.421	1.715	1.711	1.739
Ca	0.076	0.046	0.075	0.026	0.030	0.025	0.019	0.023	0.010	0.008	0.012	0.028	0.025	0.028	0.028	0.027	0.014	0.034	0.015	0.018	0.015
Σ	4.002	4.003	4.012	4.001	4.005	4.002	3.991	4.000	3.989	3.990	3.986	4.012	4.018	4.023	4.017	4.021	3.973	3.987	4.038	4.040	4.051
Fs	18.8	18.2	19.4	23.2	24.9	24.9	21.3	22.7	21.7	21.8	21.5	16.4	16.9	17.0	17.1	17.1	24.9	25.6	15.9	16.1	15.8
En	77.3	79.4	76.9	75.5	73.6	73.9	77.7	76.2	77.8	77.8	77.9	82.2	81.8	81.6	81.5	81.6	73.9	72.7	83.3	83.0	83.5
Wo	3.9	2.4	3.7	1.3	1.5	1.2	1.0	1.1	0.50	0.40	0.60	1.4	1.3	1.4	1.4	1.3	1.2	1.7	0.80	0.90	0.70

Table 8. Non- or disequilibrated clinopyroxenes

	Shaw 1	Shaw 2	Shaw 3	Jelica 1	Jelica 2	Jelica 3	Leedey 2	Leedey 3	Bjurbole 1	Bjurbole 3	Mt. Browne 1	Mt. Browne 2	Mt. Browne 3	Beamers 3	Cavour 1	Cavour 3	Olivenza 1	Olivenza 2	Plainsco 1	Plainsco 2	Plainsco 3
SiO_2	53.1	53.4	53.4	55.4	55.0	54.6	55.00	54.8	53.2	54.4	51.6	53.5	51.7	54.8	53.6	53.9	53.1	53.8	53.6	53.65	53.5
Al_2O_3	1.16	1.28	0.97	0.44	0.47	0.35	0.43	0.44	2.71	1.48	5.6	1.78	6.2	0.47	0.54	0.52	1.4	0.79	0.49	0.53	0.58
TiO_2	0.33	0.33	0.27	0.40	0.41	0.36	0.43	0.42	0.42	0.34	1.31	0.54	1.18	0.49	0.49	0.50	0.80	0.75	0.46	0.45	0.49
Cr_2O_3	1.01	1.09	0.93	0.59	0.60	0.59	0.54	0.51	1.13	0.69	1.10	0.96	1.13	0.68	0.62	0.95	0.95	1.30	0.58	0.56	0.64
FeO	8.4	7.3	7.3	5.25	5.3	6.7	4.3	4.3	9.1	5.8	3.97	3.89	4.0	4.1	5.8	5.9	5.6	5.85	4.60	4.05	4.7
MnO	0.32	0.32	0.33	0.20	0.20	0.20	0.20	0.19	0.32	0.26	0.26	0.27	0.25	0.23	0.24	0.23	0.20	0.24	0.21	0.22	0.21
MgO	17.6	17.8	17.9	16.45	16.5	15.2	15.8	15.5	19.05	17.7	15.5	16.7	15.6	16.7	16.4	16.6	15.5	15.3	16.4	16.1	15.8
CaO	18.2	17.7	18.15	21.3	21.6	21.1	22.4	22.65	13.3	18.3	20.8	21.9	20.75	21.6	21.3	21.4	21.6	21.3	22.7	22.9	22.7
Na_2O	0.35	0.48	0.38	0.50	0.45	0.41	0.52	0.49	0.51	0.69	0.80	0.57	0.77	0.52	0.47	0.45	0.54	0.39	0.51	0.55	0.54
Total	100.47	99.75	99.63	100.53	100.53	99.51	99.62	99.30	99.74	99.66	100.94	100.11	101.58	99.59	99.46	99.13	99.69	99.72	99.55	99.01	99.16

OXYGEN ON BASIS OF 6(O)

	Shaw 1	Shaw 2	Shaw 3	Jelica 1	Jelica 2	Jelica 3	Leedey 2	Leedey 3	Bjurbole 1	Bjurbole 3	Mt. Browne 1	Mt. Browne 2	Mt. Browne 3	Beamers 3	Cavour 1	Cavour 3	Olivenza 1	Olivenza 2	Plainsco 1	Plainsco 2	Plainsco 3
Si	1.952	1.965	1.968	2.012	2.002	2.017	2.015	2.015	1.946	1.986	1.845	1.953	1.856	2.004	1.981	1.967	1.960	1.985	1.977	1.985	1.982
Aℓ	0.050	0.056	0.042	0.019	0.020	0.015	0.019	0.019	0.017	0.064	0.278	0.077	0.262	0.020	0.024	0.023	0.061	0.034	0.021	0.023	0.025
Ti	0.009	0.009	0.008	0.011	0.011	0.010	0.012	0.012	0.012	0.009	0.035	0.015	0.032	0.014	0.014	0.014	0.022	0.021	0.013	0.013	0.014
Cr	0.026	0.028	0.024	0.015	0.016	0.016	0.014	0.013	0.029	0.018	0.028	0.025	0.029	0.018	0.016	0.017	0.025	0.034	0.015	0.015	0.017
Fe	0.258	0.225	0.225	0.160	0.161	0.207	0.132	0.132	0.278	0.177	0.119	0.119	0.120	0.125	0.179	0.184	0.174	0.181	0.142	0.125	0.147
Mn	0.010	0.010	0.010	0.006	0.006	0.006	0.006	0.006	0.010	0.008	0.008	0.008	0.008	0.007	0.008	0.007	0.006	0.008	0.007	0.007	0.007
Mg	0.965	0.976	0.983	0.891	0.895	0.837	0.863	0.850	1.0386	0.963	0.831	0.909	0.835	0.910	0.904	0.920	0.853	0.842	0.902	0.880	0.872
Ca	0.717	0.698	0.717	0.829	0.842	0.835	0.879	0.892	0.521	0.716	0.797	0.857	0.798	0.846	0.844	0.853	0.854	0.842	0.897	0.908	0.901
Na	0.025	0.034	0.027	0.035	0.032	0.029	0.034	0.035	0.036	0.049	0.055	0.040	0.054	0.037	0.034	0.032	0.039	0.028	0.037	0.040	0.039
$\sum$	4.013	4.001	4.005	3.978	3.985	3.972	3.976	3.974	3.988	3.989	3.995	4.002	3.993	3.982	4.002	4.016	3.994	3.974	4.010	4.003	4.003
Fs	13.3	11.8	11.7	8.5	8.5	11.0	7.0	7.1	15.1	9.5	6.8	6.3	6.9	6.7	9.3	9.4	9.2	9.7	7.3	6.5	7.7
En	49.7	51.4	51.1	47.4	47.1	44.5	46.0	45.3	56.5	51.9	47.6	48.2	47.6	48.3	46.9	47.0	45.4	45.1	46.4	46.2	45.4
Wo	37.0	36.8	37.2	44.1	44.4	44.5	47.0	47.6	28.4	38.6	45.6	45.5	45.5	45.0	43.8	43.6	45.4	45.2	46.2	47.3	46.9

Table 9. Calculated values for ionic distributions in ortho- and clinopyroxenes for T = 1073° K (800° C)

F_1	F_2	X_{Fe}^{opx}	F_3	F_4	X_{Fe}^{cpx} (Wo = 0.46)	X_{Fe}^{cpx} (Wo = 0.45)	X_{Fe}^{cpx} (Wo = 0.44)
0.04	0.1841	0.1120	0.0464	0.6213	0.0480	0.0543	0.0605
.12	.4247	.2724	.1374	.8430	.1024	.1108	.1193
.20	.5751	.3876	.2260	.9078	.1493	.1584	.1675

$X_{Fe}^{opx}/X_{Mg}^{opx}$	$X_{Fe}^{cpx}/X_{Mg}^{cpx}$ (Wo = 0.46)	$X_{Fe}^{cpx}/X_{Mg}^{cpx}$ (Wo = 0.45)	$X_{Fe}^{cpx}/X_{Mg}^{cpx}$ (Wo = 0.44)
0.126	0.098	0.110	0.121
.374	.234	.252	.271
.633	.382	.404	.427

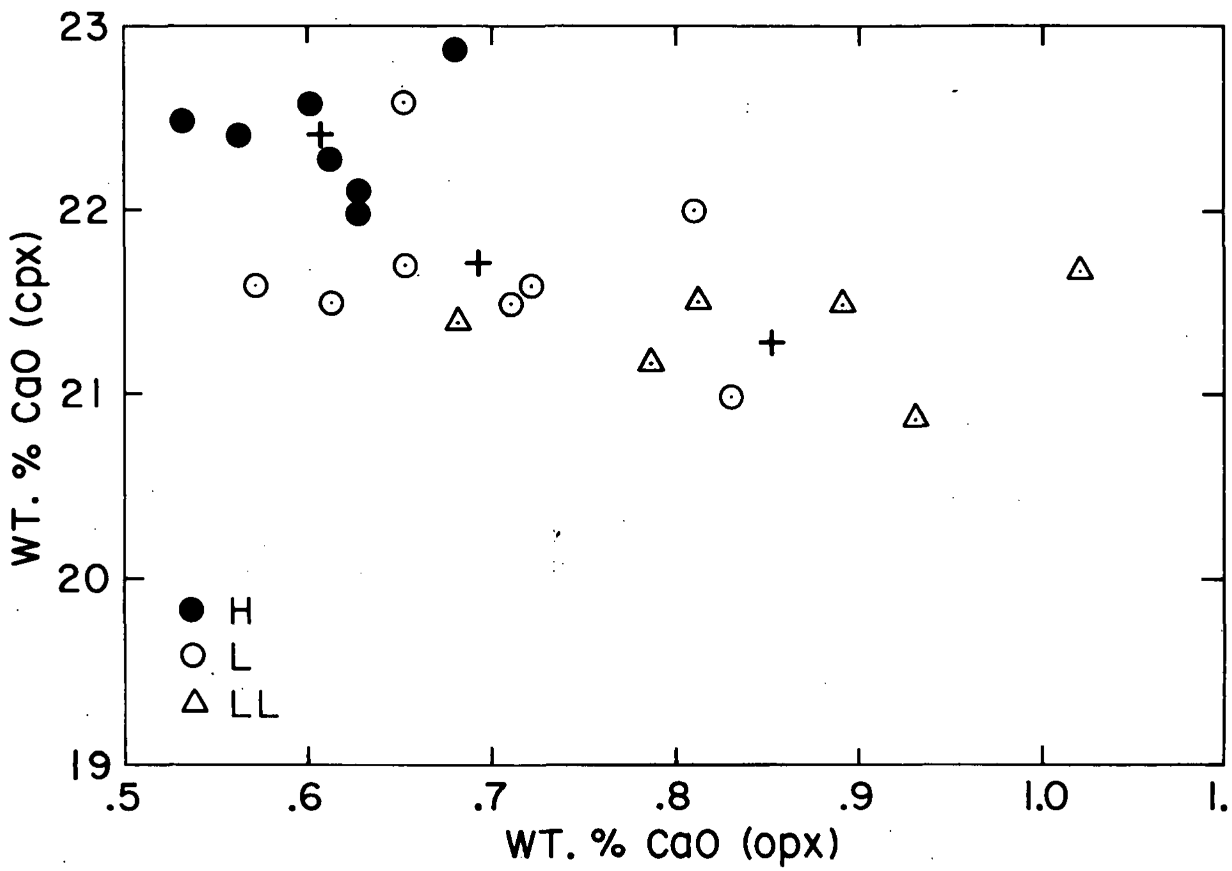

Fig. 1. Weight percent CaO in cpx vs. opx. Crosses indicate average CaO for each group.

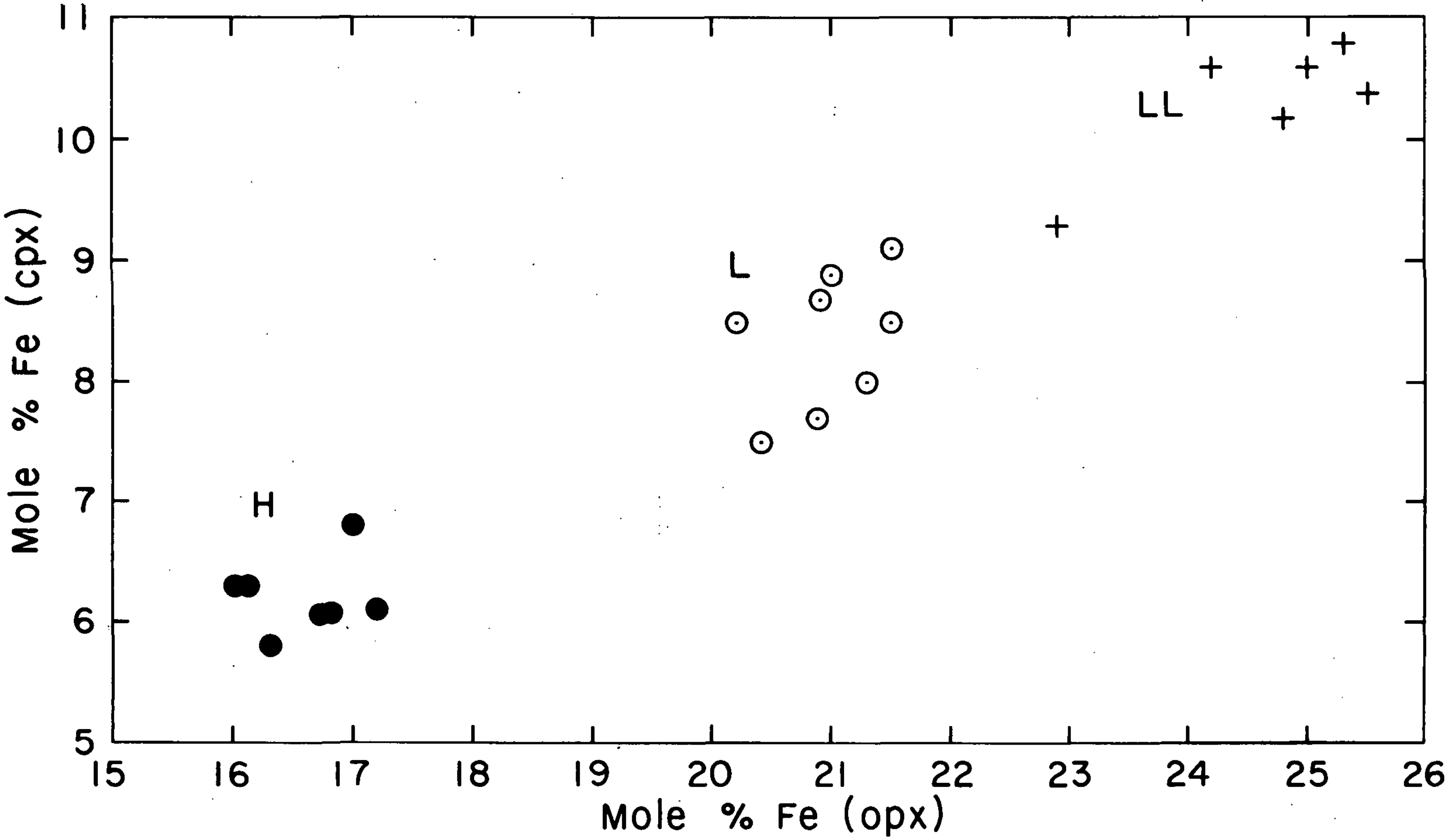

Fig. 2. Mole percent Fe in cpx vs. opx that illustrate clustering of pyroxenes for each group.

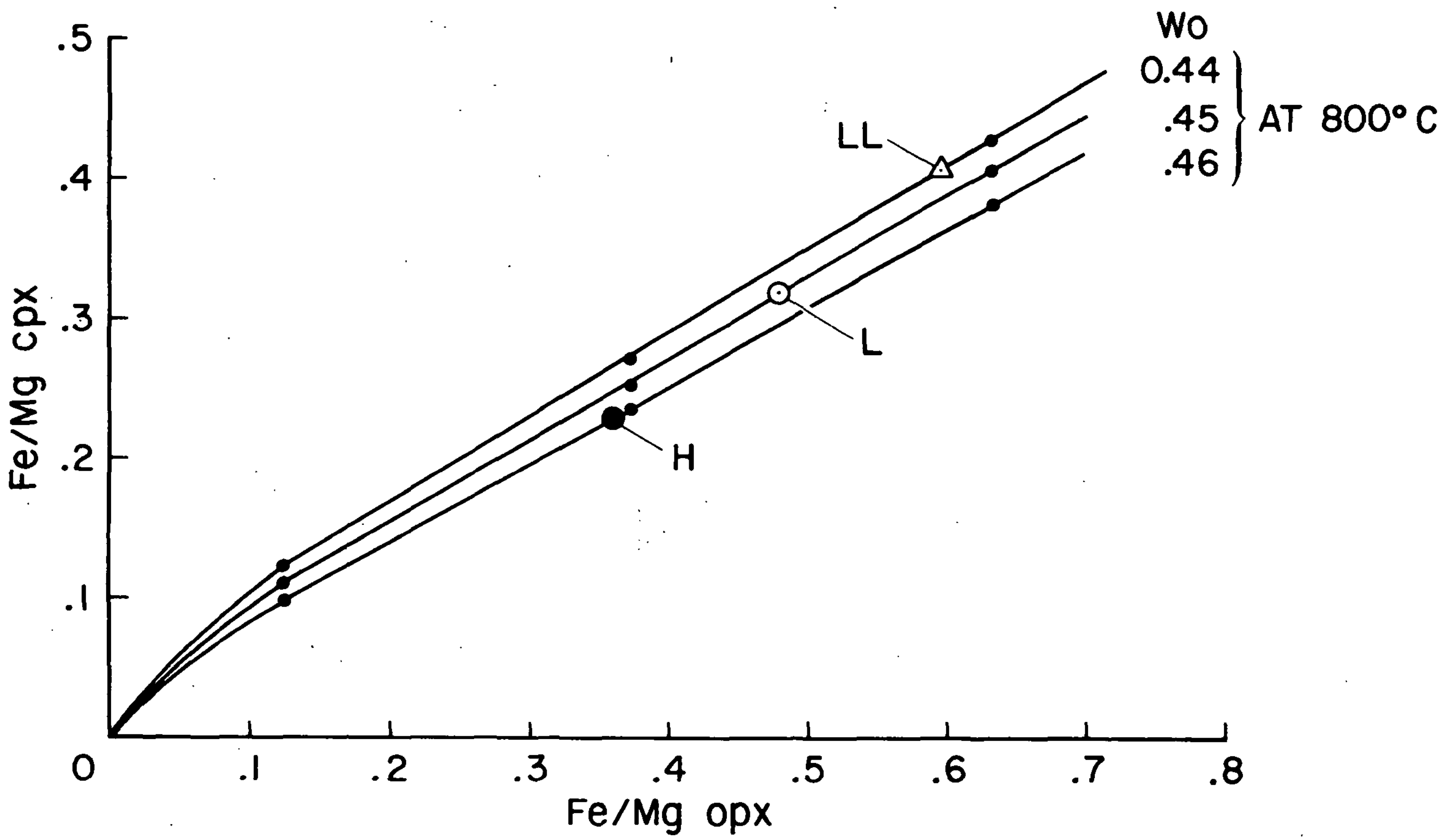

Fig. 3. Linear plot of average compositions for H, L, and LL pyroxenes and a construction curve for each group average Wo content calculated from the Blander model for an assumed temperature of 800° C.