

Manganese Thermometer for Mantle Peridotites

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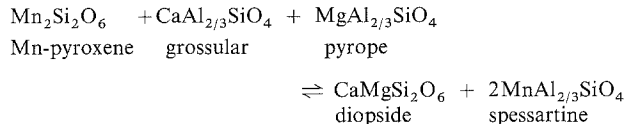
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Abstract. The temperature dependence of the Mn-Mg distribution between garnet and clinopyroxene, originally proposed by Carswell, was confirmed by Shimizu and Allègre (1978) using ion microprobe and electron microprobe data. High precision electron microprobe analyses of a larger set of 52 lherzolites from S. Africa and Malaita, Solomon Islands show considerable scatter in the temperature dependence of this distribution, and correlation with the CaO content of the garnet is indicated. A new distribution coefficient is based on the reaction:



It was calibrated against temperature determined from two independent thermometers (Wells pyroxene and O'Neill-Wood garnet-olivine) for lherzolitic assemblages, and shown to be sensitive to within $\pm 50^\circ\text{C}$ for most specimens in the range $900^\circ\text{--}1,300^\circ\text{C}$. This distribution coefficient appears independent of pressure within the uncertainty of the available data, and has the potential to be a third independent thermometer for use in garnet lherzolites and possibly eclogites.

Introduction

As part of a general program to investigate the distribution of trace elements among minerals from the upper mantle, systematic analyses are being made of nodules transported to the Earth's surface by kimberlite and other magmas.

Substitution of Mn for Mg in coexisting garnet and clinopyroxene depends on temperature (Carswell 1974; Jawardena and Carswell 1976; Shimizu and Allègre 1978), but the data sets were too small to

provide a definitive calibration. We now report electron microprobe data for the Mn/Mg/Fe/Ca distributions between coexisting garnet and clinopyroxene in many lherzolite nodules from S. African kimberlites (specimens described in Nixon and Boyd 1973a and b and Bishop et al. 1978) and from the Malaita alnöite, Solomon Islands (Nixon and Boyd 1979; Delaney et al. 1979). Examination of the new data set suggests that the Mn distribution between coexisting garnet and clinopyroxene depends on the grossular content of the garnet as well as on the temperature. A new exchange reaction which involves Ca as well as Mn and Mg is calibrated against two independent geothermometers; the Wells (1977) modification of the Wood-Banno two-pyroxene scheme, and the O'Neill and Wood (1979) garnet-olivine experimental thermometer. These calibrations are compared with the experimental observations on Mn distribution by Wood (1976) and Finnerty (1977), and with thermochemical calculations using tabulated calorimetric data.

Review

Carswell (1974, Fig. 4) found that the ratio

$$(X_{\text{Mn}}/X_{\text{Mg}})_{\text{gt}}/(X_{\text{Mn}}/X_{\text{Mg}})_{\text{cpx}}$$

decreased fourfold for garnet lherzolites as the temperature inferred from the Ca/(Ca+Mg) ratio of the clinopyroxene increased from 800° to $1,300^\circ\text{C}$. The wide scatter of data probably results from low analytical precision for Mn in the clinopyroxene and the simplicity of the pyroxene thermometer. A further attempt to use this distribution on charnockitic minerals (Jayawardena and Carswell 1976) led to a discrepancy of 200°C with other temperature estimates.

Shimizu and Allègre (1978), as part of an ion-microprobe study of garnet lherzolite nodules in kimberlites, obtained a good correlation between $(\text{Mn}/\text{Mg})_{\text{cpx}}/(\text{Mn}/\text{Mg})_{\text{gt}}$ and $\text{Ca}/(\text{Ca} + \text{Mg} + \text{Fe})_{\text{cpx}}$ for 11 specimens, which they compared with a temperature range of $1,000^\circ\text{--}1,450^\circ\text{C}$ from the pyroxene thermometer calibrated by Davis and Boyd (1966).

Table 1 (Continued)

	JVS 73-155B				JVS 73-158				JVS 73-164				JVS 73-165			
	ol	gt	opx	cpx	ol	gt	opx	cpx	ol	gt	opx	cpx	ol	gt	opx	cpx
P ₂ O ₅	0.008	0.010	0.003	0.000	0.015	0.039	0.009	0.000	0.016	0.039	0.004	0.000	0.019	0.021	0.003	0.000
SiO ₂	42.0	41.5	58.0	55.0	41.5	42.2	58.6	56.6	42.3	42.0	59.0	55.0	40.9	40.93	58.2	54.0
TiO ₂	0.002	0.03	0.008	0.008	0.013	0.12	0.052	0.013	0.028	0.29	0.116	0.27	0.024	0.27	0.11	0.32
Al ₂ O ₃	0.014	20.0	0.70	1.34	0.02	21.8	0.84	2.42	0.029	20.7	0.89	2.4	0.014	21.2	0.92	3.33
Cr ₂ O ₃	0.026	4.91	0.28	1.21	0.03	4.13	0.33	1.86	0.031	4.21	0.37	2.19	0.027	4.15	0.35	2.43
FeO	6.71	6.3	3.94	1.67	7.64	7.12	4.42	2.26	6.75	6.64	4.35	2.25	6.90	6.27	4.18	2.18
MnO	0.078	0.301	0.09	0.065	0.09	0.334	0.097	0.073	0.09	0.351	0.106	0.074	0.087	0.353	0.098	0.075
MgO	51.0	20.4	36.5	17.5	51.0	21.6	35.6	16.5	50.0	20.69	35.0	15.6	52.0	21.8	35.9	15.5
NiO	0.35	N.D.	0.08	0.034	0.26	0.0	0.066	0.027	0.40	0.01	0.11	0.04	0.45	0.000	0.12	0.06
CaO	0.02	5.27	0.46	20.7	0.025	4.80	0.483	19.8	0.025	4.98	0.45	20.0	0.03	4.58	0.47	18.2
Nb ₂ O	0.003	0.010	0.06	0.98	0.007	0.04	0.127	1.99	0.010	0.057	0.13	2.33	0.004	0.07	0.16	2.89
K ₂ O	n.a.	N.D.	n.a.	0.016	n.a.	0.000	n.a.	0.016	n.a.	0.00	n.a.	0.013	n.a.	n.a.	n.a.	n.a.
Total	100.211	98.731	100.121	98.523	100.600	102.183	100.624	101.559	99.679	99.967	100.526	100.167	100.455	99.644	100.511	98.985
°C	OW, 948; W 1033				OW, 997; W 981				OW, 916; W, 866				OW, 998; W 921			

	JVS 73-172A				JVS 73-185			
	ol	gt	opx	cpx	ol	gt	opx	cpx
P ₂ O ₅	0.010	0.017	0.006	0.000	0.011	0.034	N.D.	N.D.
SiO ₂	41.0	42.0	59.0	54.0	41.8	41.4	58.0	54.2
TiO ₂	0.032	0.20	0.13	0.31	0.006	0.06	0.02	0.04
Al ₂ O ₃	0.012	20.7	0.72	2.73	0.016	18.6	0.84	2.48
Cr ₂ O ₃	0.024	4.32	0.26	1.66	0.035	7.96	0.45	2.40
FeO	9.15	7.98	5.3	3.10	6.31	5.84	3.95	1.89
MnO	0.098	0.335	0.115	0.089	0.09	0.328	0.106	0.072
MgO	49.1	19.8	34.0	16.1	51.3	20.3	35.0	16.0
NiO	0.304	N.D.	0.09	0.041	0.35	0.01	0.10	0.043
CaO	0.022	5.24	0.46	18.7	0.023	5.78	0.48	19.0
Nb ₂ O	0.008	0.039	0.13	2.01	0.009	0.03	0.14	2.14
K ₂ O	n.a.	0.003	n.a.	0.027	n.a.	0.000	n.a.	0.016
Total	99.760	100.634	100.211	98.767	99.950	100.342	99.086	98.281
°C	OW, 1020; W, 984				OW, 971; W, 1004			

^a Center of zoned grain
n.a.: Not analyzed; N.D.: Not detected
JVS 73-63, 64, 76: Bultfontein Floors, S. Africa
JVS 73-105, 106: Frank Smith mine, S.A.
JVS 73-149 to 185: Matsoku, Lesotho.

Table 2. New electron microprobe analyses of F.R. Boyd's specimens

	FRB-348				FRB-349				FRB-350				FRB-351			
	gt	ol	opx	cpx	gt	ol	opx	cpx	gt	ol	opx	cpx	gt	ol	opx	cpx
P ₂ O ₅	0.036		0.001	0.004	0.018		0.000	0.007	0.013		0.003	0.005	0.056		0.005	0.007
SiO ₂	44.0	42.2	58.7	55.8	43.0	42.4	59.4	54.0	42.0	42.0	58.0	55.4	42.0	42.0	59.0	55.0
TiO ₂	0.02		0.01	0.01	0.04		0.03	0.07	0.06		0.05	0.12	0.02		0.01	0.02
Al ₂ O ₃	22.0		0.81	1.94	21.8		0.79	2.89	21.3		0.99	2.80	20.7		0.90	1.58
Cr ₂ O ₃	3.76		0.26	1.38	3.07		0.22	1.85	3.29		0.25	1.94	4.21		0.31	1.49
FeO	7.20	7.9	4.95	2.08	7.55	7.8	4.56	2.19	8.1	8.0	4.76	2.15	6.55	7.5	4.86	1.93
MnO	0.374		0.11	0.065	0.409		0.099	0.062	0.463		0.12	0.069	0.339		0.10	0.067
MgO	17.91	51.0	35.64	15.97	20.0	51.0	36.39	15.0	19.9	51.5	35.12	15.4	20.05	51.0	36.0	16.8
NiO	0.00		0.12	0.05	0.00		0.09	0.01	0.01		0.07	0.044	0.00		0.10	0.07
CaO	5.25		0.44	21.19	4.69		0.22	19.21	4.97		0.26	19.46	5.56		0.44	20.26
Na ₂ O	0.013		0.07	1.36	0.019		0.062	2.22	0.02		0.057	2.24	0.018		0.071	1.31
K ₂ O	N.D.		n.a.	0.009	N.D.		n.a.	0.008	N.D.		n.a.	0.003	N.D.		n.a.	0.012
Total	100.563	101.1	101.111	99.858	100.596	101.2	102.419	97.517	100.126	101.5	99.68	99.631	99.503	100.5	101.796	98.544
T °C	OW, 848; W, 925				OW, 865; W, 904				OW, 816; W, 926				OW, 1008; W, 996			
	PHN-1559B				PHN-1566				PHN-1567				PHN-1568			
	gt	ol	opx	cpx	gt	ol	opx	cpx	gt	ol	opx	cpx	gt	ol	opx	cpx
P ₂ O ₅	0.013	0.013	0.005	0.015	0.012		0.014	0.022	0.021		0.011	0.021	0.014		0.003	0.019
SiO ₂	41.0	41.0	58.0	55.0	40.8	40.6	55.8	42.03	41.5	58.0	54.63	41.5	42.0	57.5	55.8	55.8
TiO ₂	0.03	0.002	0.01	0.01	0.91		0.29	0.012	0.004	0.01	0.03	0.009	0.000	0.000	0.01	0.01
Al ₂ O ₃	19.3	0.014	0.87	1.84	18.5		2.3	21.5	0.026	0.89	1.7	19.4	0.022	0.84	2.9	2.9
Cr ₂ O ₃	6.68	0.031	0.39	1.95	5.54		0.80	3.6	0.022	0.39	1.34	7.40	0.015	0.37	1.94	1.94
FeO	7.25	8.28	4.92	2.32	8.4	11.15	5.31	6.9	6.5	4.04	1.58	6.32	6.56	4.18	1.97	1.97
MnO	0.406	0.118	0.13	0.091	0.239		0.132	0.380	0.104	0.095	0.061	0.431	0.09	0.102	0.058	0.058
MgO	19.0	50.1	35.0	16.11	20.9	47.4	21.0	20.16	51.0	35.5	16.7	18.97	50.7	35.7	16.1	16.1
NiO	0.00	0.408	0.11	0.04	0.01		0.06	0.004	0.385	0.10	0.03	0.00	0.423	0.09	0.044	0.044
CaO	5.72	0.024	0.49	19.08	4.66		13.12	5.59	0.019	0.32	21.88	6.15	0.016	0.31	19.61	19.61
Na ₂ O	0.015	0.006	0.11	1.60	0.066		1.38	0.014	0.003	0.06	1.5	0.02	0.003	0.05	2.38	2.38
K ₂ O	N.D.	n.a.	n.a.	0.02	N.D.		0.03	N.D.	n.a.	n.a.	0.01	0.009	n.a.	0.006	0.011	0.011
Total	99.414	99.996	100.035	98.076	100.037	99.15	100.236	100.212	100.230	99.407	99.472	100.230	99.843	99.151	100.842	100.842
T °C	OW, 945; W, 1021				OW, 1388; W, nu				OW, 823; W, 816			OW, 879; W, 924				

Table 2 (Continued)

	PHN-1597				PHN-1610				PHN-1611				PHN-1924			
	gt	ol	opx	cpx	gt	ol	opx	cpx	gt	ol	opx	cpx	gt	ol	opx	cpx
P ₂ O ₅	0.026		0.012	0.009	0.025	0.012	0.008	0.008	0.027	0.013	0.019	0.005	0.019		0.010	0.005
SiO ₂	42.0	41.1	58.0	55.4	42.0	41.0	55.5	42.0	42.0	40.5	56.0	55.5	42.0	41.0	57.7	54.7
TiO ₂	0.56		0.12	0.19	0.86	0.026	0.31	0.61	0.61	0.026	0.204	0.31	0.54		0.11	0.19
Al ₂ O ₃	20.4		1.33	2.6	21.5	0.067	2.39	22.0	22.0	0.070	1.37	2.4	21.3		1.2	2.59
Cr ₂ O ₃	2.24		0.34	0.79	2.03	0.023	0.36	1.28	1.28	0.041	0.219	0.49	2.68		0.23	0.93
FeO	6.6	9.41	5.38	4.17	9.21	11.7	5.6	9.0	9.0	11.5	7.17	5.38	6.59	8.91	4.93	3.62
MnO	0.200		0.13	0.134	0.251	0.131	0.142	0.142	0.232	0.124	0.130	0.113	0.274		0.130	0.118
MgO	22.0	49.7	33.4	22.0	20.77	47.0	20.7	21.0	21.0	47.5	32.0	20.2	23.52	49.4	33.5	19.8
NiO	0.009		0.12	0.07	0.02	0.32	0.07	0.07	0.003	0.354	0.104	0.06	0.006		0.103	0.07
CaO	4.14	0.105	1.58	12.43	4.43	0.106	12.87	4.39	4.39	0.116	1.44	13.88	4.30		1.3	14.02
Na ₂ O	0.066		0.39	1.64	0.07	0.031	1.39	0.064	0.064	0.038	0.314	1.5	0.069		0.3	1.83
K ₂ O	N.D.		n.a.	0.05	0.006	n.a.	0.03	0.03	N.D.	n.a.	n.a.	0.03	0.007		n.a.	0.03
Total	98.241	100.315	100.802	99.483	100.312	100.416	99.370	100.606	100.606	100.282	98.97	99.868	101.305	99.31	99.513	97.903
T °C	OW, (1625); W, 1371				OW, (1278); W, nu				OW, 1282; W, 1298				OW, (1646); W 1277			
	PHN-1925				PHN-2001				PHN-2302A				PHN-2549			
	gt	ol	opx	cpx	gt	ol	opx	cpx	gt	ol	opx	cpx	gt	ol	opx	cpx
P ₂ O ₅	0.022	0.005	0.010	0.007	0.021	0.008	0.013	0.009	0.009	0.013	0.013	0.00	0.010	0.023	0.00	0.006
SiO ₂	42.0	40.8	58.0	55.5	42.5	41.0	59.0	54.4	54.4	41.4	41.2	56.77	55.41	41.0	58.01	55.0
TiO ₂	0.78	0.021	0.17	0.30	0.73	0.024	0.16	0.28	0.28	0.05	0.10	0.016	0.045	0.10	0.02	0.06
Al ₂ O ₃	20.23	0.048	1.29	3.01	21.0	0.046	1.1	2.3	2.3	19.7	7.0	0.70	2.56	20.0	0.71	2.75
Cr ₂ O ₃	2.43	0.051	0.30	0.94	2.5	0.033	0.24	0.90	0.90	7.17	7.0	0.38	2.87	5.20	0.35	1.85
FeO	6.98	9.49	5.69	4.03	7.17	9.33	5.5	3.32	3.32	6.33	7.0	4.35	2.16	6.66	4.67	2.45
MnO	0.268	0.12	0.131	0.134	0.293	0.116	0.13	0.118	0.118	0.38	0.38	0.12	0.08	0.326	0.109	0.082
MgO	22.0	49.8	34.0	19.85	21.0	49.0	34.4	18.8	18.8	20.46	51.4	36.5	16.7	21.0	35.5	16.18
NiO	0.02	0.367	0.12	0.07	0.005	0.371	0.101	0.06	0.06	0.01	0.025	0.12	0.06	0.01	0.11	0.05
CaO	4.11	0.075	1.31	13.51	4.47	0.058	1.04	16.21	16.21	6.14	0.025	0.46	18.77	4.60	0.50	19.65
Na ₂ O	0.11	0.052	0.44	2.20	0.07	0.018	0.22	1.53	1.53	0.023	0.03	0.13	2.43	0.03	0.15	1.84
K ₂ O	0.01	n.a.	n.a.	0.033	N.D.	n.a.	n.a.	0.04	0.04	0.005	0.01	0.01	0.018	0.005	0.006	0.03
Total	98.96	100.829	101.461	99.580	99.759	100.004	101.904	97.967	97.967	101.681	99.625	99.556	101.113	98.954	100.129	99.948
T °C	OW, (1443); W, 1274				OW, (1345); W, 1202				OW, 1005; W, 987				OW, 962; W, 974			

Table 2 (Continued)

	PHN-2557/5				PHN-2575/2				PHN-2575/3			
	gt	ol	opx	cpx	gt	ol	opx	cpx	gt	ol	opx	cpx
P ₂ O ₅	0.012	Np	0.00	0.007	0.017	n.a.	0.003	0.005	0.021	n.a.	0.003	0.001
SiO ₂	42.5		58.0	55.5	43.0		57.3	54.5	41.5		57.04	55.0
TiO ₂	0.011		0.00	0.01	0.54		0.09	0.14	0.71		0.18	0.29
Al ₂ O ₃	22.0		0.67	1.33	21.7		1.07	1.87	21.0		1.20	2.11
Cr ₂ O ₃	3.51		0.24	1.04	2.58		0.29	0.77	2.21		0.28	0.75
FeO	6.81		4.40	1.92	7.15		5.86	3.94	6.88		5.78	4.03
MnO	0.318		0.10	0.066	0.265		0.133	0.130	0.243		0.129	0.124
MgO	22.36		35.4	17.62	22.0		32.7	20.01	22.0		33.0	19.89
NiO	0.02		0.14	0.07	0.02		0.123	0.08	0.02		0.123	0.07
CaO	5.37		0.51	22.30	4.39		1.45	14.91	4.23		1.43	13.99
Na ₂ O	0.004		0.06	1.07	0.05		0.27	1.33	0.07		0.34	1.66
K ₂ O	N.D.		0.004	0.04	0.006		0.006	0.04	0.005		0.005	0.033
Total	102.915		99.524	100.973	101.718		99.295	97.725	98.889		99.51	97.948
T °C	OW, nu; W, 902				OW, nu; W, 1280				OW, nu; W, 1291			

n.a.: Not analyzed

N.D.: Not detected

Np: Not present

OW: O'Neill-Wood; W: Wells; nu: thermometer not usable because a mineral is absent

FRB-348 to 351: Bulfontein Floors, S. Africa (Boyd and Nixon, 1976)

PHN-1559B, 1924, 1925, 2001: Mothae, Lesotho (Nixon and Boyd, 1973a)

PHN-1566 to 1611: Thaba Putsoa, Lesotho (Nixon and Boyd, 1973a)

PHN-2302A: Liphobong, Lesotho (Nixon and Boyd, 1973b)

PHN-2557/5, 2575/2, 2575/3: Letseng-La-Terae, Lesotho (Bloomer and Nixon, 1973)

^a Center of zoned grain

Table 3. Comparison of present electron microprobe analyses (DSDN) with ion microprobe analyses by Shimizu and Allègre (1978) and routine electron microprobe analyses by F.R. Boyd

Specimen	Mineral	TiO ₂ ppmw			Cr ₂ O ₃ wt. %			MnO ppmw			Reference
		DSDN	Boyd	SA	DSDN	Boyd	SA	DSDN	Boyd	SA	
PHN 1569 ^a	gt	190	400	230	7.99	7.43	5.09	4,430	4,600	3,740	(a)
	cpx	200	100	150	1.30	1.70	1.30	660	700	650	
PHN 1611 ^a	gt	8,370	8,000	7,670	1.28	1.46	1.53	2,320	2,600	2,070	(a)
	cpx	3,100	3,000	2,800	0.49	0.49	0.46	1,130	1,300	1,050	
PHN 1925	gt	7,800	8,000	7,610	2.43	2.57	1.93	2,740	2,400	2,170	(a)
	cpx	3,000	3,100	2,700	0.94	0.86	0.67	1,180	1,400	960	
PHN 2302A	gt	800	800	1,360	7.17	6.39	6.07	3,800	3,800	3,490	(b)
	cpx	450	500	510	2.87	2.81	2.40	800	600	670	
FRB 348	gt	200	<300	310	3.76	3.79	3.33	3,740	3,800	3,100	(c)
	cpx	100	<300	100	1.38	1.32	1.51	650	600	660	

^a Inhomogeneous (Boyd and Finger, 1975)

(a) Nixon and Boyd (1973a); (b) Nixon and Boyd (1973b); (c) Boyd and Nixon (1976)

Table 4. New MnO analyses and estimated temperatures for specimens analyzed by Bishop et al. (1978)

Number	740	749	794	1,140	1,143B	1,149	1,156	1,352	1,359
Weight % MnO garnet	0.355	0.030	0.317	0.390	0.512	0.359	0.473	0.604	0.375
Weight % MnO cpx	0.093	0.067	0.124	0.069	0.109	0.097	0.126	0.077	0.093
°C (Wells)	1,002	—	1,007	839	828	933	1,033	735	951
°C (O'Neill-Wood)	1,040	1,016	1,125	863	826	983	1,034	—	986
Number	1,361	1,362	1,363	1,755	1,870/2	2,014/1	2,125	BT7	
Weight % MnO garnet	0.427	0.431	0.437	0.484	0.400	0.487	0.380	0.354	
Weight % MnO cpx	0.126	0.117	0.116	0.076	0.063	0.060	0.109	0.094	
°C (Wells)	958	986	976	776	—	—	994	929	
°C (O'Neill-Wood)	1,019	1,007	—	—	833	926	1,114	978	

Finnerty (1977) synthesized coexisting clinopyroxene and garnet, and found that Mn tends to move from clinopyroxene to garnet with falling temperature. However direct comparison with the present data is not possible because of absence of complete chemical analyses for the synthetic minerals. The synthesis data of Akella and Boyd (1974) and of Wood (1976) are qualitatively consistent with the distributions observed in natural lherzolites, but exact comparison is not possible because of compositional differences between synthetic and natural minerals.

Samples and Analytical Techniques

Electron microprobe analyses of silicates from 17 lherzolite and pyroxenite nodules from southern African kimberlites (Bishop et al. 1978) were augmented by new analyses for 14 lherzolite nodules measured with the same standards (Table 1). F.R. Boyd, Jr., kindly provided grain mounts of minerals from 27 nodules from S. African kimberlites. New analyses are given in Table 2, five of which allow a cross-check of the analyses made by Shimizu and Allègre (Table 3). New silicate analyses for three garnet lherzolite nodules from the Malaita alnöite were cross-checked with routine analyses made by F.R. Boyd, Jr. (Nixon and Boyd 1979).

Analytical techniques at Chicago were described by Bishop et al. (1978). Routine analyses in Table 1 are given to one decimal place for numbers greater than 10 wt. % and two decimal places for

numbers less than 10. Special analyses of high precision are given to three decimal places, and are precise to 20–50 ppmw (2σ). Some analyses of MnO in Bishop et al. (1978) were made with routine procedures accurate only to ± 0.02 wt. % MnO (1σ) and were replaced by new analyses of higher precision (Table 4). All electron microprobe analyses of MnO listed in this paper are precise to ± 40 ppm (2σ), except for the routine analyses by F.R. Boyd, Jr., for which the accuracy is probably 200 ppmw (1σ). The Chicago analyses were standardized against synthetic Corning glass *W* with 0.50 wt. % Mn (atomic absorption analysis by Jun Ito decreased). Special care was taken to obtain reliable analyses of CaO and MgO in the clinopyroxene, and data from spectrometer and solid-state-detector methods were cross-checked. The standard was synthetic diopside.

All the lherzolite nodules contain coarse mineral grains, and the chemical compositions are uniform within experimental error except for small variations in some elements (especially Al and Cr) of some minerals. These variations were always less than 10% of the amount present, and for brevity a mean value is reported for analyses made on several spots. All analyses for Mn were consistent for each grain within experimental error.

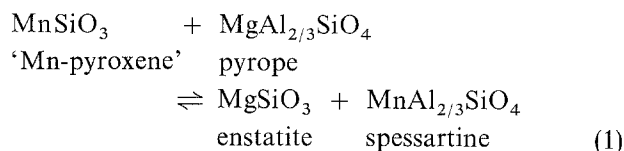
In general, there is good agreement between the Chicago and Boyd analyses when account is taken of the lower precision for minor elements in the latter.

No clear trends emerge in the comparison of electron and ion microprobe analyses in Table 3, especially as two specimens are known to be inhomogeneous particularly for Cr. The cali-

bration of ion microprobe analyses is still a matter of great difficulty because of poor understanding of the physics of the sputtering process. Particularly serious is the effect of the matrix on the sputtering yield, as for example the strong effect of the Fe/Mg ratio of olivine on the yields of ions of transition metals (Shimizu et al. 1978; Steele and Hutcheon 1979). Whereas Shimizu and Allègre (1978) suggest an error of 5% for their ion microprobe analyses of Cr and Mn, and 10% for Ti, the data in Table 3 may indicate a rather larger value. In particular, their analyses of Mn in both garnet and clinopyroxene average about 11% lower than the present electron-microprobe analyses. A detailed comparison of electron and ion microprobe analyses on exactly the same spots is needed to provide definitive data. Such comparisons at Chicago with an ARL-EMX electron microprobe and an AEI ion microprobe have indicated that it is difficult to obtain ion microprobe analyses *accurate* (not *precise*) to better than 10–20%, and indeed the simplest interpretation of Table 3 is that the analyses from the CAMECA ion microprobe have a similar level of accuracy.

Model Reactions for Mn Distribution, and Empirical Calibration

The distribution of Mn and Mg between garnet and clinopyroxene may be represented by an exchange reaction between components as follows:



for which an equilibrium constant K_1 may be defined as

$$K_1 = \frac{X_{\text{en}}}{X_{\text{rh}}} \cdot \frac{X_{\text{spess}}}{X_{\text{py}}}$$

Since data are available for rhodonite and not 'Mn-pyroxene', we use that mineral since Navrotsky and Coons (1976) suggest that ΔH and ΔS between pyroxenoid and pyroxene are small. If all the Mg in clinopyroxene is assigned to an enstatite component, Eq. (2) is equivalent to the distribution coefficients used by Carswell and (inverted) by Shimizu and Allègre. The exchange reaction assumes that Mn substitutes for Mg in the clinopyroxene structure with Ca (and other substituents) being unaffected.

Shimizu and Allègre (1978) found a linear trend for $K_D^{\text{Mn}} = (\text{Mn}/\text{Mg})_{\text{cpx}}/(\text{Mn}/\text{Mg})_{\text{gt}}$ vs. $\text{Ca}/(\text{Ca} + \text{Mg} + \text{Fe})_{\text{cpx}}$. Our Fig. 1 for this plot shows a scatter of up to ± 0.1 in K_D , or up to 0.04 in $\text{Ca}/(\text{Ca} + \text{Mg} + \text{Fe})_{\text{cpx}}$, about the line drawn by Shimizu and Allègre, but our data for specimens studied by Shimizu and Allègre do fall close to the line. The increased scatter results from the use of a larger set of specimens and cannot

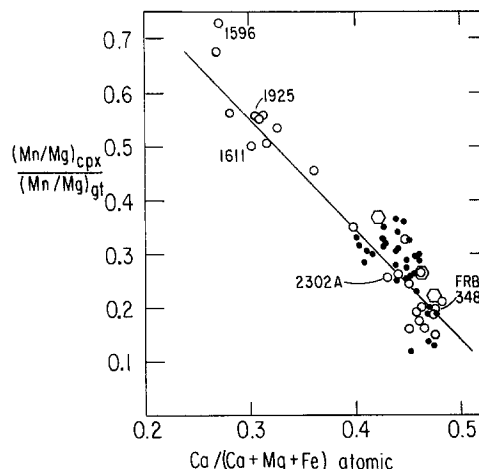


Fig. 1. $(\text{Mn}/\text{Mg})_{\text{cpx}}/(\text{Mn}/\text{Mg})_{\text{gt}}$ vs. $\text{Ca}/(\text{Ca} + \text{Mg} + \text{Fe})_{\text{cpx}}$ for data in Table 1 (filled circle) and Table 2 (open circle) for S. African specimens and in Delaney et al. (1979) for Malaita specimens (hexagon). The straight line is from Shimizu and Allègre (1978, Fig 1). Labeled specimens were analyzed by Shimizu and Allègre, and cross-checked at Chicago (Table 3)

be ascribed to experimental error. There is no thermochemical reasons for the relationship to be linear, and indeed for an Arrhenius dependence of K_D with $1/T$ the plot should be asymptotic to $\text{Ca}/(\text{Ca} + \text{Mg} + \text{Fe}) = 0.5$.

Arrhenius plots are shown in Fig. 2 for two independent estimates of temperature. The Wells (1977) thermometer is a modification of the two-pyroxene thermometer developed by Wood and Banno (1974) and depends largely on the variation of the $\text{Ca}/(\text{Ca} + \text{Mg} + \text{Fe})$ ratio of the clinopyroxene, and partly on the assignment of minor elements to the $M1$ and $M2$ sites. It is based partly on experimental data for the pyroxene quadrilateral and partly on crystal-chemical theory. Because the solvus approaches the diopside composition rather closely below $1,100^\circ\text{C}$, it is extremely important to obtain an accurate value for the ratio $\text{Ca}/(\text{Ca} + \text{Mg})$ of the clinopyroxene. Electron microprobe analyses made by F.R. Boyd and at Chicago gave $\text{Ca}/(\text{Ca} + \text{Mg} + \text{Fe})$ ratios which agreed to a mean value of 0.006. It is extremely difficult to obtain electron microprobe analyses of elemental ratios accurate to better than 0.5% when account is taken of statistical counting errors in both the standard and unknown. Certainly the electron microprobe error is trivial for temperatures above $1,200^\circ\text{C}$, but it is quite significant for temperatures below $1,000^\circ\text{C}$ where the analytical uncertainty can become equivalent to $\sim 50^\circ\text{C}$.

The O'Neill and Wood (1979) thermometer depends on the Fe/Mg distribution between olivine and garnet. The calibration is based on experimental measurements for Mg-rich compositions up to

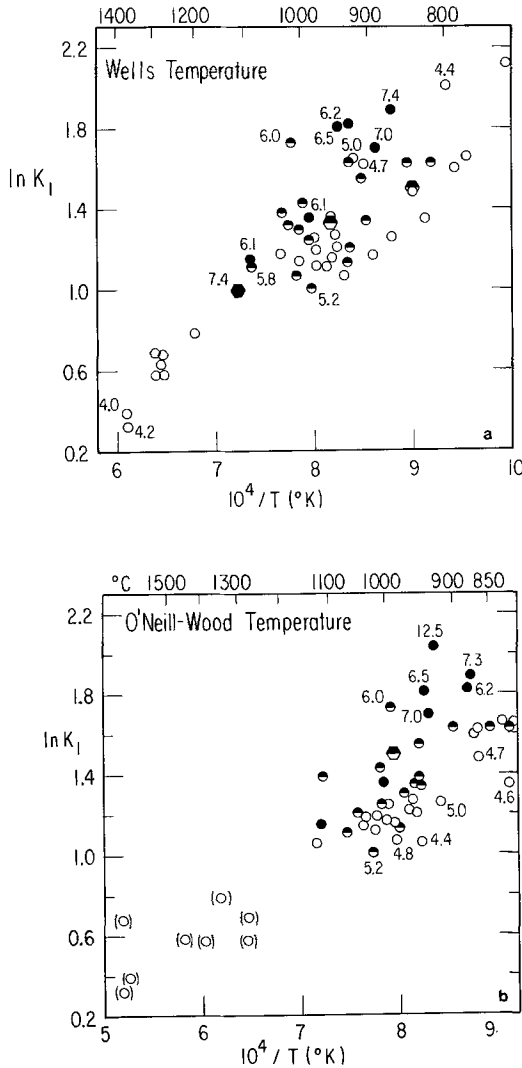


Fig. 2a and b. $\ln K_1$ vs. Wells two-pyroxene temperature (a) and O'Neill-Wood garnet-olivine temperature (b). CaO content of garnet indicated by symbols: *open symbol*, 4–5 wt.%; *half-open symbol*, 5–6 wt.%; *filled symbol*, over 6 wt.%. The CaO contents are listed for some extreme specimens. *Brackets* are placed around symbols for O'Neill-Wood temperatures above the range of good calibration. *Circles* and *hexagons*, respectively, denote S. Africa and Malaita

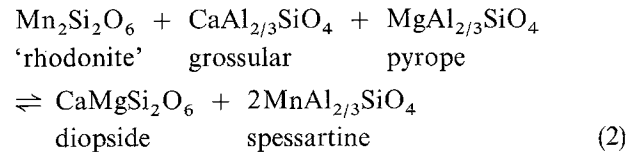
1,400°C, and is particularly useful below 1,200°C where the two-pyroxene thermometer becomes less precise. Listed temperatures above 1,200°C for the O'Neill-Wood thermometer are definitely subject to an unknown extrapolation, and we consider the Wells thermometer to be more useful for temperatures above 1,200°C.

For the overlapping temperature range of 1,200°–1,000°C, temperatures from these two independent thermometers agree mostly within 50°C. Lack of knowledge of the $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio produces systematic displacements in both thermometers.

Although there is a distinct tendency for $\ln K_1$ to increase with falling temperature using both the Wells and O'Neill-Wood calibrations, there is a large scatter especially for temperatures below 1,100°C. The scatter is larger than expected from just the analytical error, and a matrix effect or effects was suspected. No significant correlation was found for Fe and Al. The symbols in Fig. 2 are ornamented with three levels of CaO content in the garnet, and a weak trend is indicated. One specimen (2014/A) with 12.5 wt.% CaO in the garnet stands out in Fig. 2b. Unfortunately the trend is not completely systematic and some other effect or effects as yet unknown may be responsible. Because of the strong correlation between CaO and Cr_2O_3 contents in garnet a similar but weaker trend was found when the latter element was plotted.

A new thermometer was developed as follows to take account of the possible effect of CaO.

Use of the K_1 ratio implicitly assumes that all the Mn enters the *M1* site in the clinopyroxene, but Lindstrom and Weill (1978) showed that about half of the Mn in doped clinopyroxenes substitutes for Ca in the *M2* site and about half for Mg in the *M1* site. Accordingly a more realistic reaction may be



for which the equilibrium constant may be defined as

$$K_2 = \frac{X_{\text{spess}}^2}{X_{\text{gr}} \cdot X_{\text{py}}} \cdot \frac{X_{\text{diop}}}{X_{\text{rh}}}$$

Arrhenius plots of K_2 are shown in Fig. 3. Points for specimens with high and low CaO contents in the garnet are now *randomly* intermingled. For the Wells thermometer, the scatter is quite small above 1,100°C where the thermometer is particularly sensitive, but is rather greater at lower temperatures, especially for two specimens PHN 1570 and BD 1143B. For the O'Neill-Wood thermometer, the scatter for temperatures below 1,100°C is similar to that for the Wells thermometer, and the largest deviations are again for these two specimens. The Chicago and Boyd analyses agree well for PHN 1570, and there is no obvious explanation of the deviations. Of course, equilibrium may not have been established, but both the PHN 1570 and BD 1143B specimens are granular lherzolites with no unusual textural features. Points with O'Neill-Wood temperatures above 1,200°C are bracketed in Fig. 3b because the thermometer was not so thoroughly calibrated there. Although these

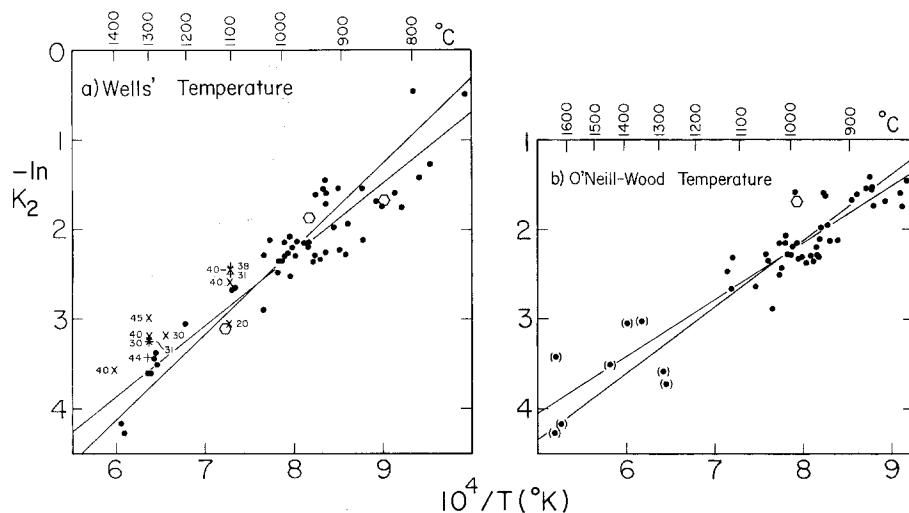


Fig. 3a and b. In K_2 vs. Wells two-pyroxene temperature (a) and O'Neill-Wood garnet-olivine temperature (b). Brackets are placed around symbols for O'Neill-Wood temperatures above the range of good calibration. Circles and hexagons, respectively, denote S. Africa and Malita. Crosses represent experimental data: horizontal (Akella and Boyd 1974); inclined (Wood 1976). The pressure is denoted in kb by the small two-figure numbers

points do not cluster as closely as the ones for the Wells thermometer, they still tend to lie at the extension of the trend for lower temperatures.

Taking the data at face value, least-square fits regressed separately on both temperature and K_D gave the following equations:

Wells thermometer

$$10^4/T = 1.0779 \cdot \ln K_2 + 10.469 \quad r = 0.93 \quad (3)$$

$$\ln K_2 = 0.8002 \cdot 10^4/T - 8.687 \quad (4)$$

O'Neill-Wood thermometer

$$10^4/T = 1.3471 \cdot \ln K_2 + 10.888 \quad r = 0.92 \quad (5)$$

$$\ln K_2 = 0.6287 \cdot 10^4/T - 7.197. \quad (6)$$

Each pair of equations is non-equivalent, as is readily seen by rewriting Eq. (4) and (6) to give Eq. (7) and (8), respectively.

$$10^4/T = 1.2497 \cdot \ln K_2 + 10.856 \quad (7)$$

$$10^4/T = 1.5907 \cdot \ln K_2 + 11.448. \quad (8)$$

Unfortunately there is no standard mathematical procedure to handle least-square fits when there are comparable errors in both variables. If the ratios of the errors can be estimated, the procedure in Smith et al. (1969), developed M.H. Hey, can be used. For the present set of data it is not possible to make objective estimates of the relative errors, and empirically we suggest the use of Eqs. (9) and (10) which have a mean gradient and pass through the intersection of the pairs of equations.

$$\text{Wells thermometer} \quad 10^4/T = 1.1638 \ln K_2 + 10.663 \quad (9)$$

$$\text{O'Neill-Wood thermometer} \quad 10^4/T = 1.4689 \ln K_2 + 11.1679. \quad (10)$$

An experimental determination of K_2 can then be converted directly into estimates of temperatures by Eqs. (9) and (10).

Empirically, the Mn distribution is apparently almost independent of pressure, as indicated by comparison between data for specimens from South Africa and Malaita, Solomon Islands. The three specimens from Malaita have estimated pressures from the pyroxene barometer considerably lower than those for the S. African specimens. Whatever the details of the calibration of the pyroxene barometer, the Malaita specimens yield pressures some 20 kb lower than those of the S. African specimens (Nixon and Boyd 1979), but have temperatures near the center of the band for the S. African specimens (Fig. 3a). Only one Malaita specimen could be plotted on Fig. 3b, and it lies inside the band but considerably displaced from the center. In the next section, thermochemical data suggests that the Mn distribution is much less sensitive to pressure than to temperature.

Comparison With Thermochemical Calculations

Using heats of formation of diopside and rhodonite (Navrotsky and Coons, 1976), spessartine (Shearer, 1973), enstatite and pyrope (Charlu et al., 1975), estimates were obtained for $\Delta H_{\text{react}}^{\circ}$ of reactions (1) and (2). For reaction 1, the calculated value of -14 J/mol has the same sign as the value of $\sim -37 \text{ kJ/mol}$ obtained from the gradient of the least-squares fit to the Arrhenius plots (Fig. 2), but is numerically smaller. For reaction 2, the calculated value of -19 kJ/mol also has the same sign as the value taken from the average slope of the regression lines in Fig. 3 but is considerably less than the graphical value of -85 kJ/mol . These large discrepancies in the numerical values reflect the non-ideal character of the Mn-Mg and Mg-Ca substitutions in pyroxenes and garnet (Holst 1978). Thus the observed trends are

more sensitive to temperature than the values estimated for the assumption of ideal solution. Lack of experimental data for Mn solution in both phases precludes more detailed modeling of the non-ideality.

For Eq. (1), molar volume data from Robie et al. (1978) and density data for a high-pressure pyroxene polymorph of MnSiO_3 (Akimoto and Syono 1972) in preference to data for rhodonite yield a value of ΔV of -0.114 J/bar (-0.027 cal/bar). The smallness of this value suggests that the effect of pressure should be negligible on the Mn/Mg distribution between garnet and clinopyroxene, as was found empirically in the preceding section.

For reaction 2, the calculated ΔV of -0.301 kJ/bar (-0.072 cal/bar) suggests a somewhat greater dependence of pressure for the Mn–Mg–Ca distribution but the effect should again be fairly small. The coefficient K_2 should increase with pressure, but again the empirical comparison between *S. African* and *Malaita* specimens does not yield a definite effect, perhaps because of swamping by various experimental errors.

Comparison With Experimental Observations

Figure 3a contains the sparse data obtained by Akella and Boyd (1974) and Wood (1976) for pressures between 20 and 45 kb and temperatures of 1,100° and 1,300°C. The combination of the two data sets provides no consistent indication of a pressure effect, but such an effect might be obscured either by scatter resulting from incomplete attainment of equilibrium or by the low precision in routine electron microprobe analyses of Mn for the fine-grained synthetic minerals.

The data points for the synthetic assemblages were plotted in Fig. 3a at the actual experimental temperature. Replacement by the Wells temperature calculated from the pyroxene compositions would cause small changes of position, but all points would remain in the general band defined by the natural specimens.

Conclusion

The present empirical data suggest that the Mn/Mg distribution between garnet and clinopyroxene provides a thermometer for deep-seated peridotites, and that the thermometer may be improved by taking account of the CaO content of the garnet. Further experimental data are needed to provide an independent calibration. The data from natural peridotites suggest that the effect of pressure is small, but

no precise values could be extracted. Any uncertainties in the Wells and O'Neill-Wood thermometers must carry over to the Mn/Mg/Ca thermometer. An obvious next step, which is now under investigation, is extension to eclogites and alpine-type peridotites. As the temperature falls below 900°C, as is probable for many specimens of these two suites, the MnO content of the pyroxene should tend to fall below 100 ppm, for which concentration range the higher sensitivity of the ion microprobe ($\sim 1 \text{ ppm}$) would be necessary. Particularly troublesome is the problem of extrapolation of the present calibrations to temperatures below 900°C, and an independent check of temperatures will be needed in order to obtain high accuracy. A further problem will be the different composition range of the garnets and clinopyroxenes from many of the eclogites since ideal-solution models are not likely to be obeyed.

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