A critical evaluation of two-pyroxene thermometry in Adirondack granulites
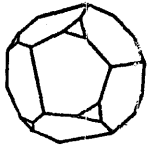
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Temperatures have been calculated from the compositions of sixty-five coexisting ortho- and clinopyroxene pairs from the Adirondacks, New York, using calibrations proposed by Wood & Banno (1973), Ross & Huebner (1975), Saxena (1976) and Wells (1977), in order to test the accuracy and precision of pyroxene thermometers in metamorphic granulites. Calculated temperatures are highly scattered (<600–900°C) and show no systematic variation within the Adirondack terrane. Several pyroxene pairs from very localized areas near Colton (N.W. Adirondacks) and Tupper Lake (C. Adirondacks) yield similar scattered temperatures (600–900°C), which disagree with feldspar and oxide thermometry and are inconsistent with the stability of various silicate and/or sulfide assemblages. All pyroxene thermometer models are sensitive to ferrous-ferric ratios with variations of up to 50°C when Fe^{3+} is estimated from pyroxene stoichiometry for pyroxene compositions obtained by microprobe analysis. These data suggest that the present pyroxene thermometers are sufficiently inconsistent, inaccurate and imprecise that they should not be used as quantitative thermometers in metamorphic rocks.

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Coexisting Ca-poor and Ca-rich pyroxenes have long been recognized as a potential geothermometer, and consequently there have been several attempts to calibrate the temperature dependence of the solution of enstatite in diopside. Boyd & Schairer (1964) and Davis & Boyd (1966) established experimentally the temperature dependence of enstatite–diopside solution, which provided the original calibration of the two-pyroxene thermometer for end-member compositions. More recently many additional experiments have been conducted on the pyroxene solvus. Warner & Luth (1974), Nehru & Wyllie (1974), Howells & O'Hara (1975), Lindsley & Dixon (1976) and Mori & Green (1975, 1976) have reported experiments with some tight reversals on the diopside–enstatite solvus. Although there is still some disagreement as to the correct solvus at different P-T, it is evident that these more recent experiments require adjustment of the Davis–Boyd solvus. Other workers have investigated different portions of the pyroxene quadrilateral. Akella & Boyd (1973) and Lindsley et al. (1974a, b) performed solvus experiments within the quadrilateral, while Lindsley & Munoz (1969) and Smith (1972) have reported on phase relations on the join ferrosilite–hedenbergite and within the iron-rich portion of the quadrilateral.

Still other workers, among them Boyd (1970), Boyd & Nixon (1973), Akella (1974), Herzberg & Chapman (1976) and Mori (1977), have examined the effect of Al_2O_3 on the solvus. Finally, Ross & Huebner (1975), Akella (1976), Mysen (1976) and Mori (1977, 1978) have attempted to determine the pyroxene solvus with experiments on natural pyroxenes only approximately represented by the quadrilateral. Despite this wealth of experimental data there are no reversed experimental data presently available on the two-pyroxene solvus at metamorphic temperatures. Consequently calibration of a two-pyroxene solvus for metamorphic rocks typically requires extrapolations of some 200°C from higher temperature experimental reversals. This extrapolation generates significant errors due to relatively wide reversal brackets at higher T and because of substantial cation ordering effects occurring in pyroxenes at metamorphic T (Saxena & Ghose 1971), which should widen the solvus relative to disordered pyroxenes. Furthermore, these experimental data indicate that the solvus is steep and insensitive to T in the metamorphic temperature range (typically 650–850°C for granulites), implying that very accurate analysis of coexisting pyroxenes is essential for accurate T estimates. Despite these potential difficulties (which also apply to a lesser degree at higher T)

there have been attempts to calibrate empirically the Ca-rich, Ca-poor pyroxene solvus for all compositions in the quadrilateral. Wood & Banno (1973) evaluated the then available experiments on the pyroxene quadrilateral and obtained an expression of T in terms of $X_{Fe^{2+}/(Fe^{2+}+Mg)}^{opx}$ and $a_{Mg_2Si_2O_6}^{pyroxene}$ in the coexisting Ca-poor *and* Ca-rich pyroxenes. They assumed an ideal two-site mixing model allowing for the blocking effect of ordered cations and assumed further that Mg and Fe^{2+} are distributed equally on M_2 and M_1. The Wood-Banno calibration has been applied in several areas (Hewins 1975; Wood 1975; Jayawardena & Carswell 1976; Wells 1976; Krogh 1977; Ormaasen 1977) with varying degrees of success. Hewins (1975) surveyed two-pyroxene data from Broken Hill and several other granulite terranes and concluded that Wood-Banno pyroxene thermometry was not only precise but accurate to $\pm 30°C$. This is a surprising conclusion in view of the approximations and extrapolations required for the empirical formulation of the thermometer.

In consideration of the more recent experiments on pyroxenes, Wells (1977) reformulated a two-pyroxene thermometer to fit the new experimental data, adapting the form of the Wood-Banno equation. Wells noted that the Wood-Banno temperatures were seriously in error for magnesian pyroxenes when compared to the later experimental data. Wells (1977) applied his thermometer to some metamorphic pyroxenes from the literature and concluded that the calculated T's were approximately correct to within 70°C. Recently Henry & Medaris (1976 and in Stormer & Whitney 1977) have modeled the Nehru-Wyllie (1974) and Lindsley-Dixon (1976) solvus data separately in a Wood-Banno type formulation.

Ross & Huebner (1975) and Saxena (1976) have taken alternate, decidedly different approaches in deriving other two-pyroxene thermometers. Ross & Huebner (1975) derived a quadrilateral solvus for pyroxenes based on composition-temperature relations of naturally occurring pyroxenes determined in part by homogenization experiments of pyroxenes containing exsolution lamellae. The homogenization experiments are unreversed and hence the precise location of the pigeonite-augite solvus may be somewhat in error. Isotherms at metamorphic temperatures ($\leq 750°C$) were empirically derived using natural augite compositions from granulite

facies rocks. Saxena, on the other hand, has theoretically modeled the activities of pyroxene components using mixing parameters inferred by Saxena & Ghose (1971). Saxena's equations for temperature calculations, based in part on compositional data from Ross & Huebner (1975) and modeling of acitivities, require successive approximations of T to be obtained with the aid of a computer program. Saxena's temperatures calculated for Bushveld pyroxenes appear to be low as he concedes. The thermometer has not been tested or widely applied in metamorphic rocks, perhaps due to the complexity of the temperature calculations.

Despite the approximations and assumptions implicit in the formulation of these pyroxene thermometers they have been applied without much critical evaluation of their internal consistency, precision or accuracy. In his calculations on published analyses of two-pyroxene granulites, Hewins (1975) neglected data from the Colton area, Adirondacks (Engel et al. 1964), near the orthopyroxene isograd (for mafic rocks), which yield Wood-Banno temperatures of 850°C, surely at least 100–150°C too high for almost any T estimate of the amphibolite–granulite boundary (i.e. Turner 1968; Miyashiro 1973; Winkler 1974; Vernon 1976). For the same Adirondack data the pyroxene thermometry of Wells (1977), which presumably should be more accurate, yields even higher temperatures of 890–920°C. Lal et al. (1978) compared Wood-Banno, Wells and the two Henry–Medaris thermometers in sapphirine granulites and found variations of up to 150°C for the same pyroxene pair. Stormer & Whitney (1977) compared several two-pyroxene thermometers with temperature data obtained from feldspars and Fe–Ti oxides in Brazilian granulites and found substantial disagreements of up to 200°C. In light of these data there is a strong suggestion that at least some of the two-pyroxene thermometers yield highly suspect results in granulites. Consequently a careful evaluation of these thermometers is necessary.

The Adirondacks are perhaps an ideal field laboratory in which to evaluate pyroxene thermometry critically. Temperature data have been obtained throughout the Adirondacks using feldspar and Fe–Ti oxide thermometry (Stormer 1975; Buddington & Lindsley 1964; see Bohlen & Essene 1977, and Fig. 1) and both thermometers are in excellent agreement. These temperature data are further substantiated and con-
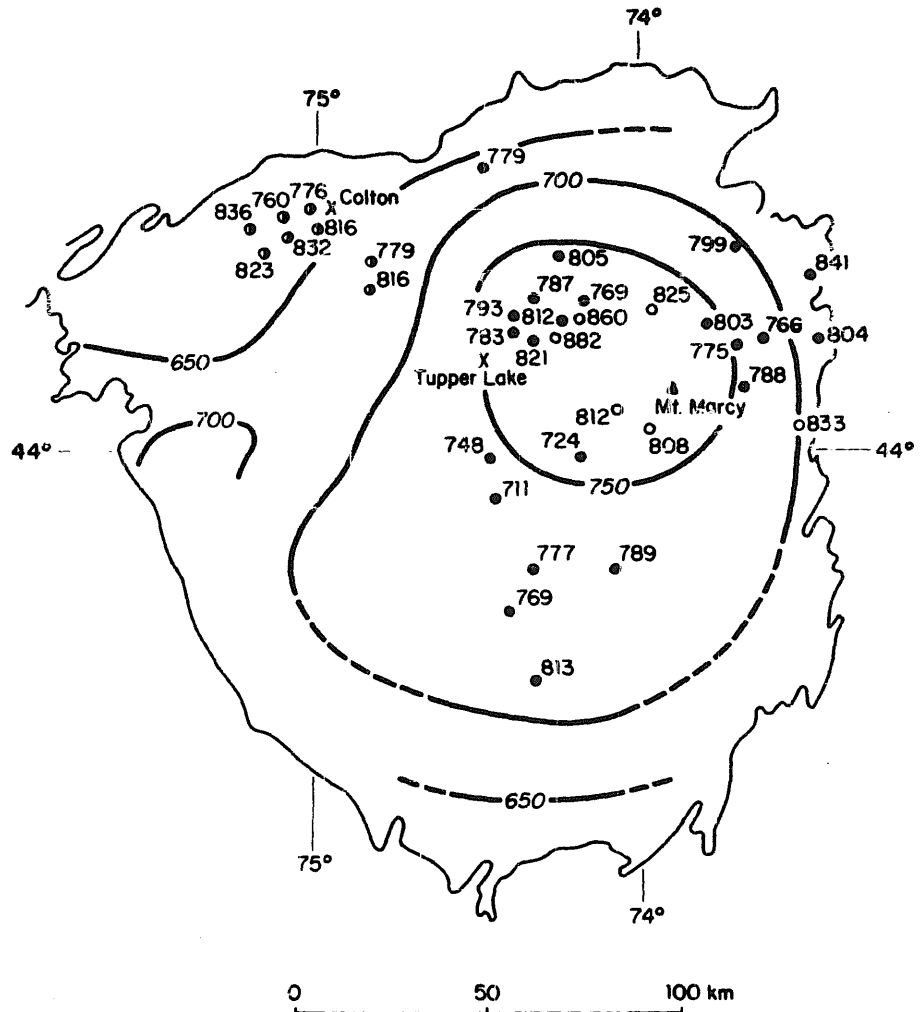
Fig. 1. Outline map of the Precambrian terrane of upper New York State showing Wood–Banno coexisting pyroxene temperatures (using estimates of Fe^{3+} as calculated from stoichiometry). ◑, ○, ● indicate data obtained by Hoffman (1979), McLelland & Whitney (1977) and Bohlen, this study, respectively. Isotherms are inferred from oxide and feldspar temperature data, after Bohlen & Essene 1977; Bohlen et al. 1979.

strained by numerous silicate or silicate–carbonate assemblages found in marbles, para- and orthogneisses throughout the Adirondacks (Valley 1977; Essene et al. 1977, 1978; Hoffman 1979; Essene & Valley 1979; Valley & Bohlen 1979) yielding a consistent temperature pattern. Not only are temperatures well known but two-pyroxene assemblages are extremely numerous to the east and southeast of the orthopyroxene isograd, located in the northwest Adirondacks (Engel & Engel 1962; Hoffman 1979). In addition there are now many analyses of Adirondack pyroxenes published by different analysts and using different analytical techniques (Engel et al. 1964; Jaffe et al. 1975; Stoddard 1976; McLelland & Whitney 1977; Hoffman 1979; Bohlen, this report) with a wide variation in Mg/ $(Mg + Fe^{2+})$, allowing tests of the compositional effect on the thermometer.

Analytical procedure

Quantitative electron microprobe analyses of coexisting ortho- and clinopyroxene were obtained using an ARL-EMX electron microprobe analyzer with wavelength dispersive LiF, PET and TAP crystal spectrometers. Spectrometer data were corrected for atomic number, fluorescence, absorption, machine drift and continuous background effects using the Fortan program EMPADR VII (Rucklidge & Gasparrini 1969). For details of standard operating conditions, standards used in analysis and additional analytical procedures the reader is referred to Bohlen & Essene (1978). Pyroxene analyses reported herein were taken from touching grains in the sections which showed textural equilibrium among all phases.

Pyroxene analyses were normalized about four cations and ferric iron was calculated from stoichiometry: $Fe^{3+} = Al^{IV} - Al^{VI} + Na + K - 2Ti$. Pyroxene data taken from other studies was also normalized in the same manner so that apparent temperature variations due to different normalization procedures were not introduced. In cases where the amount of Al was insufficient to fill the tetrahedral sites we assumed that the deficiency was a result of errors in analysis of Si, ignored it and calculated ferric iron as above (note Opx IN-2, for example). This results in slightly higher than average Fe^{3+} estimates, but inspection of Table 1 will show that pyroxenes

Table 1. Analyses of ortho- and clinopyroxene pairs from the Adirondack Highlands. Temperatures calculated from Wood–Banno assuming Fe^{3+} calculated from stoichiometry (see text).

	Opx AS-3	Cpx AS-3	Opx BM-2	Cpx BM-2	Opx BM-13	Cpx BM-13	Opx ET-1	Cpx ET-1	Opx ET-10	Cpx ET-10	Opx ET-15	Cpx ET-15
SiO_2	50.03	50.05	48.34	49.14	47.57	48.94	49.51	49.99	50.10	50.02	49.53	49.69
TiO_2	0.08	0.29	0.07	0.15	0.08	0.19	0.05	0.18	0.10	0.29	0.05	0.09
Al_2O_3	1.43	2.59	0.51	1.35	0.33	0.93	0.96	2.12	2.00	3.08	0.61	0.93
FeO	31.00	12.87	41.28	19.90	45.20	23.23	32.03	14.37	29.06	12.94	37.18	17.03
MnO	0.42	0.23	0.89	0.37	0.85	0.42	0.30	0.25	0.39	0.20	0.99	0.45
MgO	16.07	11.18	7.62	6.52	4.73	4.20	14.76	10.23	17.01	11.56	10.00	8.71
CaO	0.56	22.14	0.89	20.96	1.00	21.13	0.50	21.33	0.52	21.02	0.62	21.29
Na_2O	0.01	0.16	0.03	0.47	0.00	0.39	0.01	0.64	0.03	0.22	0.01	0.35
K_2O	0.00	0.01	0.02	0.01	0.00	0.00	0.01	0.01	0.00	0.01	0.00	0.00
Total	99.60	99.52	99.65	98.87	99.76	99.43	98.13	99.12	99.21	99.34	98.99	98.54
Si	1.950	1.907	2.001	1.948	2.010	1.965	1.975	1.919	1.943	1.905	2.020	1.950
Al	0.050	0.093	0.000	0.052	0.000	0.035	0.029	0.081	0.057	0.095	0.000	0.043
Al	0.016	0.023	0.025	0.011	0.016	0.009	0.016	0.015	0.035	0.043	0.035	0.000
Ti	0.002	0.008	0.002	0.005	0.003	0.006	0.001	0.005	0.003	0.008	0.003	0.003
Fe^{3+}	0.035	0.066	0.000	0.067	0.000	0.044	0.012	0.103	0.018	0.052	0.000	0.054
Mg	0.934	0.635	0.470	0.385	0.298	0.251	0.878	0.585	0.983	0.656	0.609	0.509
Fe^{2+}	0.976	0.344	1.429	0.593	1.597	0.736	1.056	0.358	0.925	0.360	1.269	0.505
Mn	0.014	0.007	0.031	0.012	0.030	0.014	0.010	0.008	0.013	0.007	0.035	0.015
Ca	0.023	0.904	0.039	0.390	0.045	0.909	0.021	0.877	0.021	0.858	0.028	0.895
Na	0.000	0.012	0.002	0.036	0.000	0.030	0.001	0.047	0.002	0.016	0.001	0.027
K	0.000	0.000	0.001	0.000	0.000	0.000	0.001	0.000	0.000	0.000	0.000	0.000
Wo	1.2	48.0	2.0	47.6	2.3	47.9	1.1	48.2	1.1	45.8	1.5	46.9
En	48.3	33.7	24.3	20.6	15.4	13.3	45.7	32.1	50.9	35.0	31.9	26.7
Fs	50.5	18.3	73.7	31.8	82.3	38.8	53.2	19.7	48.0	19.2	66.6	26.4
T°C	799		748		711		775		850		766	

Table 1 (continued).

	Opx ET-24	Cpx ET-24	Opx IN-2	Cpx IN-2	Opx IN-8	Cpx IN-8	Opx IN-11	Cpx IN-11	Opx LL-8	Cpx LL-8	Opx MM-18	Cpx MM-18
SiO_2	50.20	51.25	49.77	50.11	47.62	49.70	46.80	49.92	52.17	50.85	48.59	49.82
TiO_2	0.17	0.29	0.06	0.54	0.09	0.18	0.11	0.20	0.04	0.41	0.09	0.24
Al_2O_3	0.90	2.37	1.02	4.67	0.55	1.55	0.39	1.15	1.28	3.14	0.48	1.61
FeO	31.94	13.57	29.83	11.56	39.49	19.13	43.56	21.85	26.68	10.38	38.46	18.54
MnO	0.32	0.15	1.05	0.40	1.37	0.63	1.57	0.72	0.64	0.26	0.47	0.29
MgO	15.46	10.21	17.71	10.77	8.89	7.33	6.13	5.27	18.66	12.12	10.21	8.21
CaO	0.61	21.71	0.40	20.70	0.75	20.33	0.82	20.81	0.44	21.74	0.84	20.16
Na_2O	0.04	0.62	0.01	0.78	0.05	0.64	0.00	0.57	0.01	0.48	0.02	0.43
K_2O	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00
Total	99.65	100.17	99.85	99.53	98.81	99.49	99.38	100.49	99.92	99.38	99.17	99.35
Si	1.966	1.945	1.919	1.894	1.970	1.946	1.968	1.966	1.990	1.918	1.984	1.946
Al	0.034	0.055	0.046	0.106	0.027	0.054	0.019	0.034	0.010	0.082	0.016	0.054
Al	0.007	0.051	0.000	0.102	0.000	0.018	0.000	0.018	0.047	0.057	0.007	0.020
Ti	0.005	0.008	0.002	0.015	0.003	0.005	0.003	0.006	0.001	0.012	0.003	0.007
Fe^{3+}	0.019	0.033	0.050	0.031	0.025	0.074	0.012	0.048	0.000	0.036	0.005	0.056
Mg	0.903	0.577	1.017	0.607	0.548	0.428	0.384	0.310	1.061	0.682	0.622	0.478
Fe^{2+}	1.027	0.398	0.911	0.335	1.342	0.553	1.520	0.672	0.851	0.291	1.308	0.549
Mn	0.011	0.005	0.033	0.013	0.048	0.021	0.056	0.025	0.021	0.008	0.017	0.009
Ca	0.026	0.883	0.016	0.839	0.033	0.853	0.037	0.878	0.018	0.878	0.037	0.844
Na	0.002	0.045	0.008	0.057	0.004	0.048	0.000	0.044	0.003	0.035	0.002	0.036
K	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Wo	1.3	47.5	0.8	47.1	1.7	46.5	1.9	47.2	0.9	47.4	1.9	45.1
En	46.2	31.1	52.3	34.1	28.5	23.3	19.8	16.7	55.0	36.8	31.6	25.5
Fs	52.5	21.4	46.9	18.8	69.8	30.2	78.3	36.1	44.1	15.8	66.5	29.4
T°C	788		813		769		777		821		803	

Table I (continued).

	Opx N-3	Cpx N-3	Opx PH-4	Cpx PH-4	Opx SC-8	Cpx SC-8	Opx SL-5	Cpx SL-5	Opx SL-13	Cpx SL-13	Opx SL-26	Cpx SL-26
SiO_2	50.33	50.95	50.44	50.50	50.08	49.96	50.28	49.34	50.11	51.25	45.75	49.55
TiO_2	0.06	0.18	0.06	0.81	0.08	0.23	0.05	0.50	0.08	0.27	0.09	0.28
Al_2O_3	1.51	2.45	1.66	3.00	1.44	2.49	1.71	3.04	1.29	2.34	0.32	0.90
FeO	29.44	10.72	30.22	11.05	29.64	13.12	31.24	13.96	27.62	10.97	49.36	27.99
MnO	0.33	0.13	0.31	0.17	1.06	0.47	0.45	0.30	0.53	0.13	0.82	0.47
MgO	16.96	12.10	16.87	11.54	15.94	10.96	15.56	10.38	18.43	12.53	1.83	1.55
CaO	0.53	22.78	0.50	22.27	0.57	21.67	0.57	21.15	0.43	22.33	0.93	19.03
Na_2O	0.01	0.67	0.00	0.20	0.01	0.53	0.01	0.19	0.02	0.51	0.04	0.57
K_2O	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Total	99.17	99.99	100.06	99.54	98.82	99.43	99.87	98.86	98.51	100.33	99.14	100.34
Si	1.956	1.910	1.946	1.915	1.965	1.903	1.959	1.902	1.942	1.914	1.989	2.014
Al	0.044	0.090	0.054	0.085	0.035	0.097	0.041	0.098	0.058	0.086	0.011	0.000
Al	0.025	0.018	0.022	0.049	0.032	0.015	0.027	0.040	0.001	0.017	0.005	0.043
Ti	0.002	0.005	0.002	0.023	0.002	0.006	0.002	0.015	0.002	0.008	0.003	0.009
Fe^{3+}	0.015	0.110	0.028	0.004	0.000	0.109	0.000	0.042	0.055	0.090	0.004	0.000
Mg	0.983	0.676	0.970	0.652	0.933	0.622	0.904	0.597	1.065	0.697	0.119	0.094
Fe^{2+}	0.942	0.226	0.947	0.347	0.973	0.309	1.018	0.408	0.838	0.253	1.791	0.951
Mn	0.011	0.004	0.010	0.005	0.035	0.015	0.015	0.010	0.017	0.004	0.030	0.016
Ca	0.022	0.915	0.021	0.905	0.024	0.884	0.024	0.874	0.018	0.894	0.043	0.829
Na	0.000	0.048	0.000	0.014	0.001	0.039	0.000	0.014	0.002	0.037	0.004	0.045
K	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Wo	1.1	50.4	1.1	47.5	1.2	48.7	1.2	46.5	0.9	48.5	2.2	44.2
En	50.5	37.2	50.0	34.2	48.3	34.3	46.5	31.8	55.5	37.8	6.1	5.1
Fs	48.4	12.4	48.9	18.3	50.5	17.0	52.3	21.7	43.6	13.7	91.7	50.7
T°C	724		804		779		812		805		769	

Table I (continued).

	Opx SR-18	Cpx SR-18	Opx SR-29	Cpx SR-29	Opx SR-31	Cpx SR-31	Opx TL-4	Cpx TL-4	Opx W-9	Cpx W-9
SiO_2	50.52	49.76	44.96	48.52	46.94	51.00	46.66	49.03	50.30	49.48
TiO_2	0.04	0.34	0.06	0.19	0.10	0.26	0.06	0.19	0.05	0.46
Al_2O_3	1.56	2.33	0.38	0.97	0.36	1.29	0.46	1.02	1.84	3.68
FeO	30.92	13.36	48.73	23.31	43.67	23.28	42.91	23.15	28.39	12.69
MnO	0.65	0.35	0.99	0.48	0.48	0.27	1.16	0.70	0.24	0.19
MgO	15.54	10.68	2.95	5.10	7.16	5.14	7.17	5.98	17.78	11.04
CaO	0.55	21.98	0.68	19.88	0.83	19.62	0.78	19.32	0.52	20.92
Na_2O	0.00	0.19	0.01	0.61	0.00	0.51	0.00	0.61	0.01	0.38
K_2O	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01
Total	99.78	98.99	98.76	99.06	99.54	100.77	99.20	100.00	99.13	98.85
Si	1.971	1.913	1.951	1.946	1.957	2.011	1.951	1.939	1.944	1.893
Al	0.029	0.087	0.019	0.046	0.018	0.000	0.023	0.048	0.056	0.107
Al	0.043	0.019	0.000	0.000	0.000	0.050	0.000	0.000	0.028	0.059
Ti	0.001	0.010	0.002	0.006	0.003	0.008	0.002	0.006	0.001	0.013
Fe^{3+}	0.000	0.062	0.016	0.081	0.012	0.000	0.019	0.082	0.026	0.050
Mg	0.903	0.612	0.191	0.184	0.445	0.302	0.447	0.353	1.024	0.630
Fe^{2+}	1.009	0.367	1.752	0.820	1.512	0.768	1.482	0.684	0.891	0.356
Mn	0.021	0.011	0.036	0.016	0.017	0.009	0.041	0.024	0.008	0.006
Ca	0.023	0.906	0.032	0.854	0.037	0.804	0.035	0.819	0.022	0.858
Na	0.000	0.014	0.001	0.047	0.000	0.039	0.000	0.046	0.000	0.028
K	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Wo	1.2	48.1	1.6	46.0	1.9	42.9	1.8	44.1	1.1	46.5
En	46.7	32.5	9.7	9.9	22.3	16.1	22.7	19.0	52.9	34.2
Fs	52.1	19.4	88.7	44.1	75.8	41.0	75.5	36.9	46.0	19.3
T°C	787		793		783		789		841	

Table 2. Comparison of temperature data obtained using several pyroxene thermometers and feldspar and Fe–Ti oxide thermometers from assemblages found near Colton (Adirondack Lowlands), Tupper Lake and Mount Marcy (both Adirondack Highlands). Pyroxene data for Mount Marcy taken from Jaffe et al. (1975), Colton data from Stoddard (1976) and Hoffman (1979). Feldspar and Fe–Ti oxide data from Bohlen & Essene (1977) and unpublished data.

Model		Colton	Tupper Lk.	Mt. Marcy
Wood–Banno	Total Fe	746–827	764–880	722–786
	Est Fe^{3+}	759–836	769–882	746–840
Wells	Total Fe	755–872	758–883	713–817
	Est Fe^{3+}	763–878	764–900	746–872
Henry–Medaris (Nehru–Wyllie)	Total Fe	604–735	664–757	550–773
	Est Fe^{3+}	612–742	679–776	622–797
Henry–Medaris (Lindsley–Dixon)	Total Fe	611–793	694–842	629–880
	Est Fe^{3+}	622–806	716–872	638–918
Ross–Huebner	Total Fe	600–650	<600–750	600–800
	Est Fe^{3+}	<600	<600–680	<600–700
Feldspars		630–660	710–750	750
Fe–Ti oxides		insufficient data	720–790	780

with apparent Si errors are not substantially different from average calculated Fe^{3+}. Ferric iron estimates reported compare favorably with direct determinations for pyroxenes reported by Engel et al. (1964). However a 1% error in analysis of SiO_2 gives a typical error in calculated Fe^{3+} of roughly 10–40%. This in turn yields T variations of less than 40°C for most coexisting pyroxene thermometers reported below. Because of the problem of estimation of ferric iron from microprobe analyses we have calculated pyroxene temperatures (1) assuming total Fe = Fe^{2+} and (2) with Fe^{3+} calculated as above. The results and conclusions which follow are unaffected by the uncertainty in estimates of Fe^{3+}.

Analytical results and discussion

Analytical data for coexisting pyroxenes are compiled in Table 1. The temperatures given in Table 1 have been calculated using Wood–Banno and have been plotted on an outline map of the Adirondacks in Fig. 1. Inspection of Fig. 1 shows immediately that the Wood–Banno temperatures are highly variable even among pyroxene pairs obtained from closely spaced outcrops. The temperature values are generally quite high, typically 50–150°C above both oxide and feldspar temperature data. In addition comparison of Wood–Banno pyroxene temperatures across the Adirondacks suggests that metamorphic grade is not changing significantly from the northwest Lowlands to the central Highlands. However, these conclusions are contrary to the observations of other workers (Engel & Engel 1962; Buddington 1963, 1966; DeWaard 1966, 1967; Bohlen & Essene 1977; Bohlen et al. 1979; Hoffman 1979), which indicate that

metamorphic temperatures increase from the Lowlands to the Highlands but remain rather constant over broad areas of the Highlands (note the 700°C isotherm in Fig. 1). In addition, high pyroxene temperature values are wholly inconsistent with numerous phlogopite–calcite–quartz, tremolite–calcite–quartz and grossular-rich garnet–quartz assemblages found in marbles throughout the Adirondacks (Valley & Essene 1976, 1977) and also inconsistent with muscovite–quartz if the small modal amounts of muscovite (<5%) typically found in Adirondack Lowlands (northwest Adirondacks) para- and orthogneisses are primary as has been inferred by previous workers (Engel & Engel 1962; De Waard 1967). Thus it seems that the Wood–Banno thermometer is both imprecise and inaccurate in Adirondack granulites. Calculation of temperatures taking $\Sigma Fe = Fe^{2+}$ (ignoring Fe^{3+} estimations) yields somewhat lower temperatures (typically 10–30°C) but does not alter the conclusions concerning the lack of precision and accuracy. The results of other pyroxene thermometers (Wells, Henry–Medaris and Ross–Huebner) yield similarly scattered and apparently inaccurate results. Table 2 shows a comparison of the results obtained from several pyroxene thermometers with Fe–Ti oxide and two-feldspar data for three restricted localities in the Adirondacks. Analyses of twenty-one, nine and eight pyroxene pairs were obtained from areas no greater than 100 sq. km near Colton, Tupper Lake and Mount Marcy, respectively. Within these localized areas metamorphic tem-
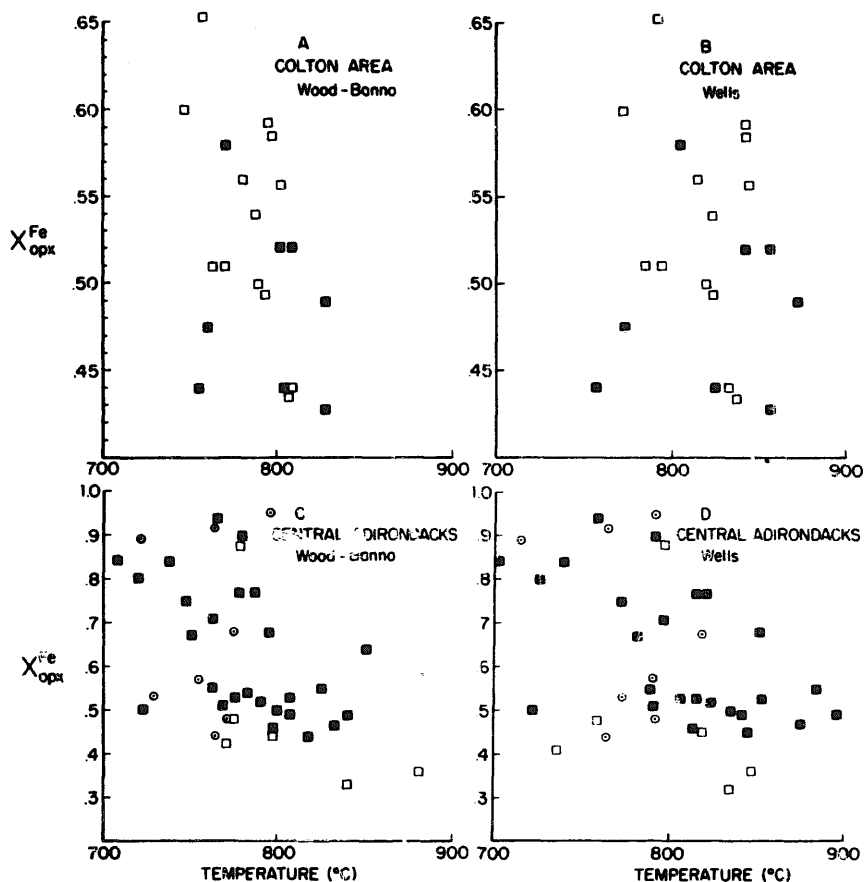
Fig. 2. Comparison of coexisting pyroxene temperatures calculated using Wood–Banno (a, c) and Wells (b, d) assuming $\Sigma Fe = Fe^{2+}$ in the northwest Adirondacks (near Colton – a, b) and in the central Adirondacks (pairs from within the 700°C isotherm, c, d). In 2a and 2b ■ and □ indicate T calculated from data by Hoffman (1979) and Stoddard (1976) respectively. In 2c and 2d ⊙, □, ■ indicate T calculated from data of Jaffe et al. (1975), McLelland & Whitney (1971) and Bohlen, this study, respectively.

peratures are presumably not varying significantly. Table 2 shows that the five pyroxene thermometers disagree among themselves by as much as 350°C and are different from the feldspar and oxide temperatures by up to 200°C. Table 2 also shows the dramatic effect estimation of Fe^{3+} content has on the calculated temperatures. Henry & Medaris (written communication, 1978) no longer consider the calibration of their pyroxene thermometers (Henry & Medaris 1976) to be correct and decided against publishing the thermometers in their present form. We shall not consider the results from the Henry–Medaris thermometers, and their use by other works is to be avoided even though the equations have been published in Stormer & Whitney (1977). The data for Wood–Banno (1973) and Wells (1977) thermometry of Colton area pyroxenes are shown in Figs. 2a and 2b, respectively. Pyroxenes were obtained from amphibolites and other ortho- and paragneisses. Note that it is not just one aberrant pyroxene pair which gives rise to the wide temperature variation listed in Table 2. Temperatures calcu-

lated for Colton pyroxenes average 788° (Wood–Banno, $\Sigma Fe = Fe^{2+}$), 799° (Wood–Banno with estimated Fe^{3+}), 819° (Wells, $\Sigma Fe = Fe^{2+}$) and 832° (Wells with estimated Fe^{3+}), 150–200°C above feldspar temperatures for the same area. Any of these pyroxene temperatures are also inconsistent with assemblages of phlogopite–calcite–quartz and tremolite–calcite–quartz found nearby (Valley & Essene 1976, 1977; Valley 1977) and biotite (annite 40–60) stability for $P_{H_2O} < P_{solid}$ conditions (Essene et al. 1978). Ross–Huebner thermometry yields temperature values which agree reasonably with feldspar and oxide data for $\Sigma Fe = Fe^{2+}$, however, when Fe^{3+} is estimated the inferred temperatures are reduced to values below 600°C, which appear to be too low. Temperatures obtained from calculations using the data of Engel et al. (1964) for pyroxenes near Colton yield distinctly higher temperatures (840–860° Wood–Banno; 890–920° Wells; 730–750° Ross–Huebner) than those calculated from the data of Stoddard (1976) and Hoffman (1979). The compositions of pyroxenes analyzed by Stoddard (1976) and Hoffman (1979)

Table 3. Analyses of a typical ortho- and clinopyroxene pair from the Colton area containing very thin, minor exsolution lamellae.

	Opx GVR-53	Cpx GVR-53	Opx GVR-53	Cpx GVR-53
			– Reintegrated –	
SiO_2	50.56	51.12	50.26	51.31
TiO_2	0.05	0.17	0.07	0.15
Al_2O_3	1.29	2.20	1.38	1.98
FeO	31.33	13.58	31.41	13.78
MnO	0.85	0.36	0.65	0.41
MgO	16.31	11.40	16.07	11.66
CaO	0.56	21.48	0.76	21.31
Na_2O	0.04	0.50	0.03	0.42
K_2O	0.00	0.00	0.00	0.00
Total	100.99	100.81	100.63	101.02
Si	1.943	1.920	1.941	1.924
Al	0.057	0.080	0.059	0.076
Al	0.002	0.017	0.004	0.012
Ti	0.001	0.005	0.002	0.004
Fe^{3+}	0.056	0.089	0.053	0.087
Mg	0.935	0.638	0.925	0.652
Fe^{2+}	0.952	0.338	0.961	0.345
Mn	0.028	0.012	0.021	0.013
Ca	0.023	0.865	0.032	0.856
Na	0.003	0.036	0.002	0.031
K	0.000	0.000	0.000	0.000
Wo	1.2	47.0	1.7	46.2
En	49.0	34.7	48.2	35.2
Fs	49.8	18.3	50.1	18.6

by electron microprobe analysis differ markedly in wollastonite content from the analyses of Engel et al. (1964), which were obtained using bulk separates. In particular the Engel et al. (1964) orthopyroxene data have 2–3 mole% greater and the clinopyroxenes 2–4 mole% less wollastonite component than similar pyroxenes analyzed by microprobe. These pyroxenes frequently show very small homogeneously distributed exsolution lamellae. Even though Engel et al. (1964) claim that they saw no exsolution lamellae in the pyroxenes they analyzed, we were concerned that analyses obtained from bulk separates yield metamorphically equilibrated compositions (including the lamellae) and the microprobe data yield post-metamorphic compositions (host compositions excluding lamellae). We have tested this by reintegrating pyroxenes with obvious, thin exsolution lamellae (using the wide-beam microprobe technique described in Bohlen & Essene 1978) and comparing their compositions with analyses of pyroxenes in the same rock which show no exsolution lamellae. Wollastonite

content of pyroxene compositions obtained using these two techniques differ by less than 0.5 mole% (see Table 3), suggesting that the microprobe analyses are giving relatively precise and accurate mineral compositions despite the minor, thin exsolution lamellae. In view of these data it seems likely that the data of Engel et al. (1964) are slightly in error probably due to small amounts (<3%) of contamination of orthopyroxene in the clinopyroxene separates and clinopyroxene in orthopyroxene splits. This would easily explain the differences in the pyroxene analyses and hence account for the dissonant temperature values calculated from compositions obtained by microprobe and bulk separate analyses.

Comparison of pyroxene thermometry data with T inferred from feldspars, oxides and silicate assemblages for Tupper Lake and Mount Marcy yield discrepancies similar to those observed for Colton data. Again the temperature values inferred from any individual two-pyroxene thermometer vary by as much as 200°C and except for a few temperatures the pyroxene thermometry does not agree well with other data. In the Mount Marcy area the assemblage monticellite–wollastonite–akermanite (Essene & Valley 1979; Valley & Essene, in preparation) fixes T = 780 ± 30°C in excellent agreement with feldspar and oxide data, yet pyroxene temperature data give widely varying and generally inaccurate results.

In addition to problems of precision and accuracy the empirically derived Wood–Banno and Wells thermometers seem also to have a compositional dependence on calculated temperatures. If the feldspar and oxide temperature data are correct then most pyroxenes within the 700°C isotherm (Fig. 1) in the central Adirondack Highlands have equilibrated at 740 ± 40°C. If we make the simplifying assumption that they are in fact isothermal and then plot T vs. X_{opx}^{Fe} (see Figs. 2c and 2d) a substantial compositional effect on T is seen, despite rather wide scatter in the data. Consideration of estimated Fe^{3+} reduces neither the scatter nor the apparent T dependence on composition. The Ross–Huebner thermometer does not appear to show a strong T-composition dependence (Fig. 3). However, the Ross–Huebner thermometer is quite sensitive to Fe^{3+} estimates and seems in either case to yield generally low temperatures. In consideration of these problems it appears that the Wood–Banno, Wells and Ross–Huebner calibrations
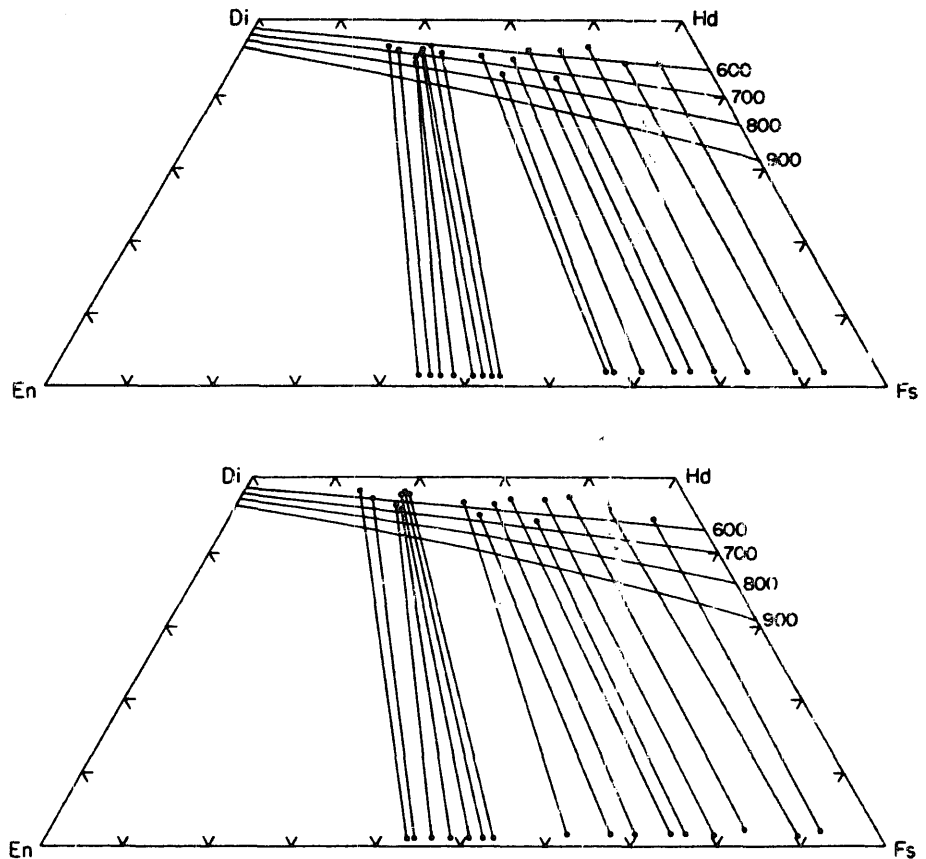
Fig. 3. Coexisting pyroxene temperatures obtained for central Adirondacks pyroxenes (pairs within the 700°C isotherm) using Ross–Huebner (1975).
(a) T obtained assuming $\Sigma Fe = Fe^{2+}$.
(b) T obtained assuming estimated Fe^{3+}.

are not useful as *quantitative* thermometers in metamorphic rocks.

We have also attempted to apply the Saxena (1976) and the Saxena & Nehru (1975) thermometers to Adirondack pyroxenes. Unfortunately the Saxena (1976) model gives no solution for many pyroxene pairs because calculations often yield the natural log of a negative number. When solutions were obtained the resultant temperature values were highly scattered (700–900°C) and extremely sensitive to Fe^{3+} estimates with temperature shifts of up to 150°C for $\Sigma Fe = Fe^{2+}$ vs. estimated Fe^{3+}. For relatively Mg-rich pyroxenes the Saxena & Nehru (1975) pyroxene thermometer (1975) also gave scattered results but generally high temperatures (815–975°C). Saxena & Nehru state that their thermometer is only approximate and should only be applied to magnesian pyroxenes. In short both the Saxena-Nehru (1975) and Saxena (1976) thermometers appear also to be inadequate for quantitative use in metamorphic terranes.

There are, no doubt, many reasons for the apparent inaccuracy and imprecision in these two-pyroxene thermometers. Surely a large portion of the uncertainty stems from a lack of experimental reversals on end-member compositions and compositions within the quadrilateral at metamorphic temperatures. The lack of tight reversals at higher T prevents accurate extrapolation to lower T. Other problems also plague these thermometers. Recently Evans & Trommsdorff (1978) and Henry & Medaris (written communication, 1979) have shown that a plot of ln K vs. 1/T for exchange of $Mg_2Si_2O_6$ in experimental solvus data is a curve rather than linear as had been previously assumed by Wood & Banno (1973) and Wells (1977). Assuming a straight-line fit results in substantial overestimation of T for pyroxenes equilibrated at metamorphic T. However, due, again, to the lack of tight reversals the location of this calibration curve is quite uncertain at low temperatures. In addition, simplifying assumptions concerning the site occupancy of Mg–Fe and the effect of additional components must also adversely affect the results. Another source of error which may be underestimated is analytical error. In addition to errors in estimated Fe^{3+}

which were discussed previously, analytical errors, especially in Ca, Mg and Fe will significantly affect the results of the two-pyroxene thermometers because of the greatly reduced T dependence of the solvus width at low temperatures.

In short, it appears that the lack of precision and accuracy of two-pyroxene thermometry in metamorphic rocks is due to several experimental, analytical and theoretical uncertainties. The results of this study indicate that two pyroxene thermometry in metamorphic rocks will at best yield only very approximate temperature data which should not and cannot be used as the only thermometer in a given metamorphic terrane.

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