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Orthopyroxene-clinopyroxene equilibria in the system $\text{CaO} - \text{MgO} - \text{Al}_2\text{O}_3 - \text{SiO}_2$ (CMAS): new experimental results and implications for two-pyroxene thermometry

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Abstract. A new set of reversal experiments for coexisting ortho- and clinopyroxenes in the system CMAS at conditions between 1,000–1,570° C and 30 to 50 kb is presented and combined with literature data. Pyroxene behaviour, particularly that of clinopyroxene, is very complicated and different styles of Al incorporation into the pyroxene structure for low and high concentrations of Al are indicated, strongly influencing the exchange of the enstatite component between ortho- and clinopyroxene. Thermodynamic modelling of this exchange is problematic because of the large number of unknown coefficients compared to the number of experiments. Thermometry based on such models becomes very dependent on accuracy of experimental data and analyses of small quantities of elements. Despite this complexity very simple empirical thermometric equations are capable of reproducing experimental conditions in the systems CMS and CMAS over a wide range of P , T conditions. We derived the equation

$$T^\circ \text{C} = 1,617 + 287.9 \cdot \ln K_D + 2.933 \cdot P$$

which gives a mean error of estimate of 25° C when applied to CMS and CMAS data.

Introduction

Two-pyroxene thermometry has received much attention ever since Davis and Boyd (1966) demonstrated the temperature dependence of the orthopyroxene-clinopyroxene miscibility gap in the simple system CaO-MgO-SiO_2 (CMS). Starting with the question of reproducing experimental conditions, best known in the form of Wood and Banno's (1973) and Wells (1977) equations (empirical thermometry), discussion has shifted towards a more complete insight in phase relationships and thermodynamic properties of pyroxenes. However even in the simplest system (CMS) there is considerable uncertainty about the correct thermodynamic model to be applied to pyroxenes (e.g. Davidson et al. 1982; Grover 1982; Holland et al. 1979; Navrotsky and Loucks 1977; Nickel and Brey 1984a; Lindsley et al. 1981).

Abbreviations used in the text: cpx = clinopyroxene; di = diopside, $\text{CaMgSi}_2\text{O}_6$; en = enstatite, $\text{Mg}_2\text{Si}_2\text{O}_6$; opx = orthopyroxene; px = pyroxene; py = pyrope; a_i^j = activity of component i in phase j ; γ = activity coefficient; $\Delta G_{P,T}(A)$ = molar Gibbs free energy difference of reaction (A) at P, T ; X_i^j = mole fraction of component i in phase j

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With the addition of only one more component, in this case Al, thermodynamically rigorous modelling procedures and expressions become drastically more complex. Accordingly error levels become higher because of combined uncertainties of numerous parameters. It is thus no surprise that even the most advanced investigations about thermodynamic properties of minerals in the system CMAS (Wood and Holloway 1984) encounter problems concerning the compatibility of calorimetric data and phase equilibrium studies. Simplifications have to be made and some empirical terms have to be introduced (e.g. Mg-Al interaction parameters of Wood and Holloway 1984). Correct thermodynamic formulation in even more complex systems will thus be of great numerical complexity and coefficients subject to high error levels. These difficulties of thermodynamic modelling are discussed. Therefore we emphasize the possibilities of empirical thermometry in the present work. Both empirical and thermodynamically constrained thermometry suffer from the unknown error introduced by extrapolation from simple to complex ('natural') systems. Empirical thermometry may derive formulations from studies in complex systems. However it is then entirely possible that the formulation was derived because of a certain bulk composition used in experiments. Thus even empirical thermometry has to prove its applicability to simple systems.

This study presents more data in CMAS and uses more recent data in CMS to update empirical two-pyroxene thermometry in these systems. It is shown that extremely simple formulations may be used to reproduce experimental conditions within reasonable limits. Formulations for rocks however will contain more correction terms for important constituents and have to rest on experiments in more complex systems (Nickel and Brey 1984b and in prep.). Nonetheless it is demonstrated that simple numerical formulations have the potential to serve as a reliable thermometer and may replace the somewhat cumbersome use of graphical methods.

Experimental strategy

As pointed out by Perkins and Newton (1980), it is very difficult to perform strict reversals in systems with more than one degree of compositional freedom. In the system CMAS it is possible to approach pyroxene equilibrium compositions from four different directions by starting with pyroxenes with low-Ca/low-Al or low-Ca/high-Al or high-Ca/low-Al or high-Ca/high-Al. For garnets either grossular-rich or pyrope-rich starting compositions are required. Following Perkins and Newton (1980) we consider it sufficient to approach equilibrium from two directions and use glassy

starting material and a mechanical mixture of pure endmembers in a set of experiments up to 50 kb. The mechanical mixture of the pure end-members pyrope (crystallized from oxide mix at 1,150° C, 35 kb) + enstatite (as clinoenstatite, synthesized from gel at 1 atm and 1,380° C for 3 days) + diopside (synthesized from glass at 1 atm and 1,250° C for 3 days) was loaded into a small Pt capsule, which was sealed by welding ("inner capsule"). The end-member mix thus has its starting points at low-Ca/low-Al orthopyroxene and high-Ca/low-Al clinopyroxene. This small container was then placed into a larger ("outer") Pt container, which contained glassy starting material. The outer capsule was also sealed by welding. The glassy starting material converts at *P* and *T* rapidly into pyroxenes of intermediate composition (Mori and Green 1975). Glassy starting material thus provides a starting point with pyroxenes low in Ca in respect to clinopyroxene and high in Ca in respect to orthopyroxene equilibrium composition. The Al-content of these initially formed intermediate pyroxenes is rather inhomogeneous, but has a strong tendency to be high or very high in Al (Howells and O'Hara 1978). Garnet nucleates with a rather grossular-rich composition and reacts towards the pyrope-rich equilibrium composition. Double-capsules of this kind were then subjected to *P*, *T* conditions. A more detailed description and a cross-section through such a double-capsule has been given by Brey and Huth (1984, Fig. 1).

Analyses demonstrate the direction and range of approach of equilibrium both in terms of Ca- and Al-content of pyroxenes. This strategy is similar to Fujii (1977), Perkins and Newton (1980), and Yamada and Takahashi (1984). The 'bracket' was established as the region of overlap in plots of Ca- vs. Al-content of the pyroxene analyses (Fig. 1a-c). There is only one condition (1,300° C, 30 kb, Fig. 1a), without compositional overlap in Ca and only two (1,300° C, 30 kb; 1,275° C, 40 kb) without overlap in Al for one or both pyroxenes. The mid-points of the compositional gaps have in these cases been used to derive the likely equilibrium value.

For two conditions (1,000 and 1,400° C, 30 kb) experiments performed in a piston-cylinder apparatus have been used. These experiments were carried out with glasses or seeded sintered oxides (see below) and constitute a half-bracket. These half-brackets have been combined with the data on crystalline starting material at 1,400° C, 30 kb from this laboratory and the data of Perkins and Newton (1980) at 1,000° C, 30 kb to establish or refine reversals (Fig. 1a).

Experimental methods

The experiments in the belt-apparatus were performed in the range from 30 to 50 kbar and 1,000–1,570° C. The belt-apparatus was calibrated at room temperature with the phase transitions of Bi, Tl and Ba and at high temperatures with the Ag-melting curve (Mirwald and Kennedy 1979) and the quartz-coesite transition (Mirwald and Masonne 1980). The accuracy and comparability of the high-temperature calibration to piston-cylinder studies has been demonstrated by Brey et al. (1983).

Pressure in the belt-apparatus is controlled automatically to within ± 300 bar. The estimated accuracy is to ± 1 kb over the entire range of temperatures (based on Mirwald and Kennedy 1979 and Mirwald and Masonne 1980). The temperature is measured with an EL18 thermocouple (Pt₇₀Rh₃₀/Pt₉₄Rh₆). Within the experimental range thermocouple drift does not pose a serious problem to the accuracy of the temperature measurement, because the drift at conditions below 1,600° C is less than 1°/h for Pt/PtRh₁₀ thermocouples (Presnall et al. 1973) and the EL18 alloy is known to have an even lower drift and is less susceptible to contamination (Koertvelyessy 1981). No correction for the effect of pressure on the emf of the thermocouple has been applied. Temperature is automatically controlled within $\pm 2^\circ$ C; its estimated accuracy is $\pm 7^\circ$ C.

The composition of the starting materials is listed in Table 1. Wide area scan analyses with the microprobe indicate a slight SiO₂ excess. Materials of composition A lie on the join between pyroxenes and garnet (identical to the composition used by Yamada

Table 1. Composition of starting materials in wt%

	A	B
SiO ₂	53.6	45.7
MgO	28.2	30.2
Al ₂ O ₃	7.4	18.3
CaO	10.8	5.8

and Takahashi 1984) and have been used in experiments with the belt apparatus. Composition B (similar to the composition used by Akella 1976) was used in piston-cylinder experiments. At 50 kb 5% H₂O was added in the runs at 1,100 and 1,200° C and about 1% H₂O at 1,300 and 1,400° C. For other experimental conditions starting material was neither specially moistened nor dried.

Composition B was prepared from pure oxide reagents. The oxides were ground together in an agate mortar under acetone and sintered in a 1 atm furnace at 990° C overnight. For another set of experiments a part of the sintered oxide mix was converted to a glass by melting on a iridium-strip heater. Pre-synthesized pure pyrope, enstatite, diopside and spinel were added to both mixtures, each seed mineral as 1% of the mix.

These runs were carried out using a 0.5 inch piston cylinder apparatus at the Geology Department, University of Tasmania (Australia). The techniques were similar to those described by Green and Ringwood (1967) for Taic-Pyrex assemblages. Temperatures were measured using a Pt/Pt₉₀Rh₁₀ thermocouple and controlled to within $\pm 7^\circ$ C of the set point.

Starting material was filled into Pt (for the experiments at 1,400° C) or Ag₅₀Pd₅₀ capsules, which were subsequently sealed by welding. For the 1,000° C runs water was sealed into the capsule (app. 5–10 wt%) to serve as a flux. Several runs of varying duration (1–24 h at 1,400° C, 24–98 h at 1,000° C) were performed in this manner. Shorter run durations resulted in greater inhomogeneity of Al₂O₃ contents in pyroxene, strong compositional zoning of minerals and smaller grain size.

Run products from these synthesis experiments were analysed using an energy-dispersive system with a JEOL-JXA 50A microprobe. All analyses were made at 15 kV and 2.1 10^{-9} A (EDAX detector, calibrated on spec pure Cu). The beam has a spot mode diameter < 1 microns. Run products from experiments of the belt apparatus were analysed with an ARL-SEM-Q microprobe (Kevex energy dispersive system). The ARL probe was calibrated with more than 20 international mineral standards.

Results

Run products have generally a typical subsolidus texture with polygonal to lobate mosaics of pyroxenes and garnet. The grain size is variable and dependent on temperature and run time, correlating positively with both. This is only a general trend and within any run there is a range in grain-sizes, only the maximum grain-sizes are different. The range is generally between 3 and 50 μ m, garnets may however be as large as 100 μ m. The composition of the Pyrope-Grossular garnets are given and discussed elsewhere (Brey et al. in prep.).

The width of the brackets is shown in Fig. 1. The values for the mid-points of brackets are listed in Table 2.

Two-pyroxene thermometry

The data base

In CMAS a number of studies have been published both in the spinel- as well as in garnet stability field (Akella 1976; Benna et al. 1981; Bruno and Facchinelli 1978;

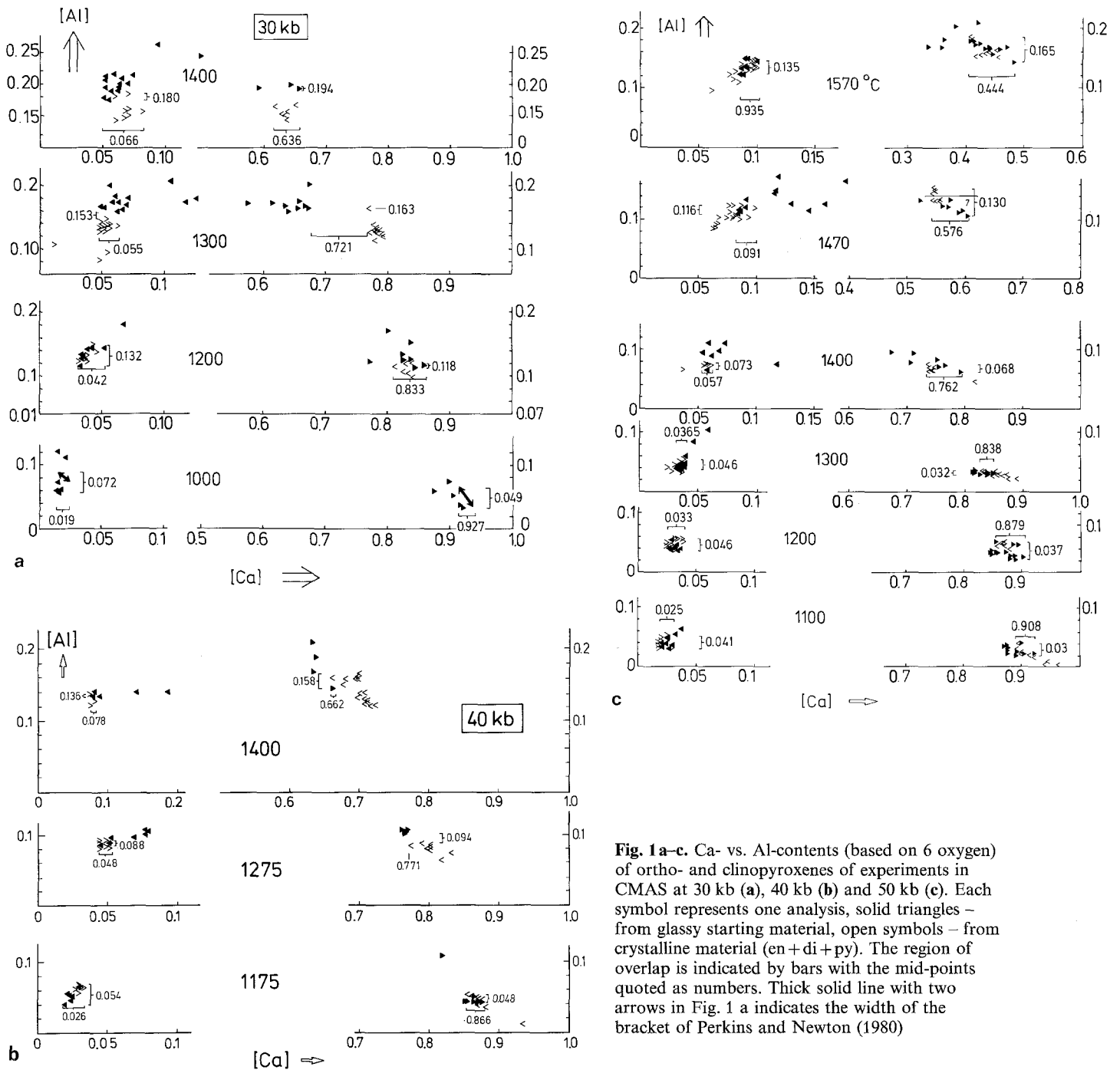


Fig. 1 a-c. Ca- vs. Al-contents (based on 6 oxygen) of ortho- and clinopyroxenes of experiments in CMAS at 30 kb (a), 40 kb (b) and 50 kb (c). Each symbol represents one analysis, solid triangles – from glassy starting material, open symbols – from crystalline material (en + di + py). The region of overlap is indicated by bars with the mid-points quoted as numbers. Thick solid line with two arrows in Fig. 1 a indicates the width of the bracket of Perkins and Newton (1980)

Dixon and Presnall 1980; Fujii 1977; Gasparik 1984; Herzberg 1978; Herzberg and Chapman 1976; Howells and O'Hara 1978; Mori 1977; Perkins and Newton 1980; Presnall 1976; Yamada and Takahashi 1984). However, only few of these data represent reversed values. The experimentalist encounters problems of reaching equilibrium by synthesis experiments in CMAS. For example Akella's (1976) data have been disputed on the basis of differing results (Howells and O'Hara 1978). Akella (1976) used a friction correction for his experimental set-up differing from those of other laboratories. Differences in results using this set-up have also been reported in a different context (Mirwald

and Kennedy 1979). The quoted pressures are therefore not directly comparable. Furthermore there are two results (1,300° C, 26 kb and 1,500° C, 31 kb of Akella 1976), where the difference in Al-contents of opx and cpx is so large that it is highly unlikely that these values represent equilibrium values for (subsolidus) ortho- and clinopyroxene.

Other studies (e.g. Herzberg 1978) are problematic because of X-ray methods of analysing clinopyroxenes and differences in analytical parameters to be used for such determinations (Benna et al. 1978). Gasparik (1984) has most recently presented data in the spinel stability field, which disagree with reversed results of Fujii (1977). This

Table 2. Mid-points of brackets of experiments in CMAS

<i>P</i> (kb)	<i>T</i> (°C)	Ca _{opx}	Al _{opx}	Ca _{cpx}	Al _{cpx}	Source
15	900	0.014	0.140	0.912	0.124	PN
16	1,000	0.029	0.204	0.911	0.183	PN
16	1,200	0.050	0.260	0.810	0.280	FU
16	1,300	0.070	0.320	0.710	0.360	FU
16	1,375	0.120	0.340	0.600	0.380	FU
20	900	0.015	0.082	0.939	0.063	PN
20	1,000	0.023	0.149	0.897	0.115	PN
22.5	1,000	0.021	0.126	0.906	0.098	PN
25	900	0.016	0.058	0.941	0.046	PN
25	1,000	0.020	0.092	0.912	0.076	PN
25	1,100	0.023	0.115	0.887	0.075	PN
30	900	0.016	0.044	0.937	0.039	PN
30	1,000	0.019	0.072	0.926	0.050	PN,NB
30	1,100	0.024	0.091	0.885	0.067	PN
30	1,200	0.042	0.132	0.833	0.118	NB
30	1,300	0.055	0.153	0.721	0.163	NB
30	1,400	0.066	0.180	0.636	0.194	NB
40	1,000	0.014	0.030	0.931	0.027	PN
40	1,100	0.015	0.049	0.906	0.037	PN
40	1,175	0.026	0.054	0.866	0.048	NB
40	1,275	0.046	0.089	0.771	0.094	NB
40	1,400	0.078	0.136	0.661	0.158	NB
50	1,100	0.025	0.041	0.908	0.030	NB
50	1,200	0.034	0.046	0.879	0.037	NB
50	1,200	0.030	0.040	0.900	0.042	YT
50	1,300	0.036	0.048	0.842	0.034	NB
50	1,300	0.044	0.051	0.840	0.063	YT
50	1,400	0.057	0.073	0.762	0.068	NB
50	1,400	0.060	0.075	0.740	0.083	YT
50	1,470	0.090	0.116	0.576	0.130	NB
50	1,500	0.090	0.107	0.640	0.112	YT
50	1,570	0.094	0.135	0.437	0.162	NB
75	1,200	0.010	0.008	0.900	0.038	YT
75	1,400	0.024	0.020	0.800	0.042	YT
75	1,500	0.052	0.032	0.720	0.042	YT
100	1,200	0.009	0.006	0.920	0.030	YT
100	1,300	0.014	0.008	0.880	0.030	YT
100	1,500	0.040	0.012	0.760	0.038	YT

Sources: *FU*: Fujii (1976); *PN*: Perkins and Newton (1980); *YT*: Yamada and Takahashi (1984); *NB*: Nickel et al. this work

may be explained by Gasparik's (1984) method of attempting a reversal: Firstly his seeds of pyroxenes on which material grew come in each case from one direction in terms of the Ca-content (high-Ca-cpx, low-Ca-opx) and are thus not reversed in this respect. Furthermore, Gasparik (1984) has not demonstrated a diffusion profile from the seeds into the grown rims, but notes that the compositional fields of the rim analyses overlap in most cases *completely*. This may indicate that the seeds were not acting as starting material but rather did act as nucleation planes for intermediate pyroxenes growing from the oxide matrix. Thus we treat the data only as half-brackets and prefer to use Fujii's (1977) reversed data at low pressures.

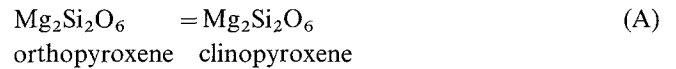
We are therefore left with only a few studies with comparable approaches of reversals: Fujii (1977), Perkins and Newton (1980), Yamada and Takahashi (1984) and this work. Within this group of experiments there are three runs (50 kb, 1,200, 1,300 and 1,400° C, Yamada and Takahashi, 1984 and this work) performed at the same conditions by different laboratories with different experimental (split

cubic anvil/belt apparatus) and analytical (JEOL-5A/ARL-SEMQ microprobe) methods which allows an evaluation of comparability. The results for orthopyroxene are very close to each other, whereas the Al-content of clinopyroxene reported by Yamada and Takahashi (1984) are higher than from our lab. Unfortunately there is little information available on the width of the brackets of Yamada and Takahashi (1984) and we do not understand this discrepancy.

In this study we used only the data of the comparable sources of reversed experiments. They are listed in Table 2 as mid-points of brackets as defined above. Some of the data had to be extracted from figures (Fujii 1977), while others were calculated from given data, assuming stoichiometry (Yamada and Takahashi (1984)).

Discussion

Geothermometry in the system CMS based on the reaction



has been discussed extensively in the literature (see review by Lindsley et al. 1982). Several plausible thermodynamic models have been put forward to explain phase relationships in this system and reproduce experimental results (e.g. Davidson et al. 1982; Lindsley et al. 1981; Navrotsky and Loucks 1977). Nickel and Brey (1984a) showed that a relatively simple thermodynamic model (independent regular solution model) is capable of both explaining phase relationships and reproducing experimental conditions over a wide range of conditions (850°–1,500° C, 2–60 kb).

These formulations may however not be applied directly to data in more complex systems such as CMAS. In CMAS there are more endmembers present (Mg-Tschemak's and Ca-Tschemak's molecules) which have to be considered. This presents a problem of the formulation of the K_D of reaction (A). In CMS the formulation

$$a_{\text{en}}^{\text{px}} = X_{\text{Mg}}^{\text{M1}} * X_{\text{Mg}}^{\text{M2}} * \gamma_{\text{en}}^{\text{px}} \quad (\text{a})$$

is numerically identical to

$$a_{\text{en}}^{\text{px}} = X_{\text{en}}^{\text{px}} * \gamma_{\text{en}}^{\text{px}} = (1-\text{Ca})^{\text{px}} * \gamma_{\text{en}}^{\text{px}} \quad (\text{b})$$

The K_D in the equilibrium expressions thus does not depend on the ordering states of the pyroxenes. In CMAS however this is no longer the case. For the disordered case the formulation (a) is still valid and may be calculated as $(1-\text{Ca}) * (1-\text{Al}/2) * \gamma$. If however the pyroxenes were completely ordered then we would need information about the mole fractions of Mg- and of Ca-Tschemak's molecule present, because then

$$X_{\text{en}}^{\text{cpx}} = 1 - X_{\text{di}} - X_{\text{MgTs}} - X_{\text{CaTs}} \quad (\text{c})$$

which is numerically equal to $(1-\text{Ca})^{\text{cpx}}$ if all Al is present as CaTs, but would have to be calculated as $(1-\text{Ca} - \text{Al}/2)^{\text{cpx}}$, if only MgTs existed within the pyroxene. While the relative difference between values obtained for an appropriately formulated $X_{\text{en}}^{\text{opx}}$ is rather small because of the low Ca-content of orthopyroxene (and often $\text{Ca} < \text{Al}$), the difference is significant for X_{en} of clinopyroxene.

In order to evaluate the question of ordering we have plotted Ca- vs. Al-content of ortho- and clinopyroxene (Fig. 2). Figure 2 shows the strong covariance of Al- and Ca-content of the equilibrium values for the pyroxenes. This is not unexpected, because the covariance of Ca and Al

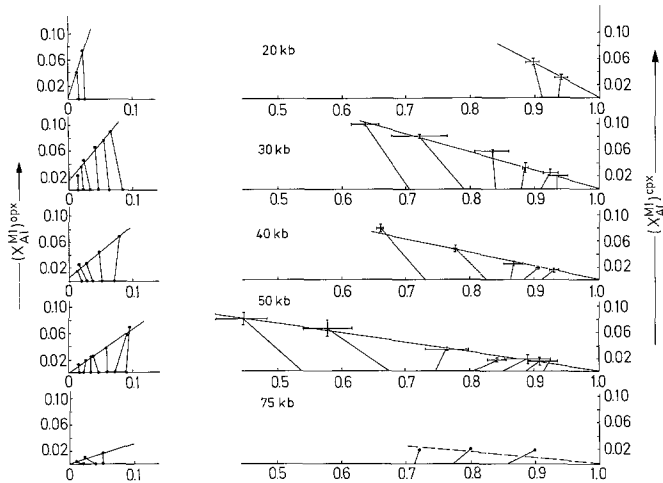


Fig. 2. Ca content vs. Al in the M1 site of the mid-points of brackets for ortho- and clinopyroxenes at 20 kb (900 and 1,000°C), 30 kb (900, 1,000, 1,100, 1,200, 1,300 and 1,400°C), 40 kb (1,000, 1,100, 1,175, 1,275 and 1,400°C), 50 kb (1,100, 1,200, 1,300, 1,400, 1,470 and 1,570°C), and 75 kb (1,200, 1,400 and 1,500°C). The error bars for clinopyroxene are the width of the brackets as derived in Fig. 1. Solid lines connect the mid-points of brackets from CMAS with the Ca-content for identical P, T conditions calculated for the Al-free system according to Nickel and Brey (1984a). Additional lines are hand-fitted isobaric Ca-Al correlations

is known within single experiments (see e.g. Fig. 1 of Perkins and Newton (1980) and this work). Ca^{++} enters at least in clinopyroxene only the M2 site and Al^{+++} only the M1 of the octahedral positions because of the large difference in volumes of sites M1 and M2 in clinopyroxene. The possibility of Ca^{++} entering the M1 site relates only to a few ppm at extremely high temperatures (Davidson et al. 1982). Thus Ca and Al should mix independently on their respective sites in the case of complete disorder. The large difference in ionic radii between Ca^{++} and Al^{+++} already suggests at least some ordering in clinopyroxene and the covariance of Ca and Al is evidence for this. In terms of thermodynamic modelling this means that any model based on a microscopic approach (hence formulating $a_{\text{en}}^{\text{px}} = X_{\text{Mg}}^{\text{M1}} * X_{\text{Mg}}^{\text{M2}} * \gamma_{\text{en}}^{\text{px}}$) has to consider the strong effect of cross-site interaction due to the reciprocal or 'internal' reaction



and in this way allow for at least some ordering or next-nearest neighbour interaction (Wood and Nicholls 1978).

Additionally shown in Fig. 2 are lines connecting the composition of pyroxenes in CMAS and CMS (from Nickel and Brey, 1984a) at a given P, T condition. This has been done to evaluate the relative partitioning between CaTs and MgTs and to indicate P, T -dependencies of reaction (B). In the case of independent mixing the ratio $(\text{Ca}/\text{Ca} + \text{Mg})_{\text{CMS}}^{\text{M2}}$ (i.e. $[\text{Ca}]_{\text{CMS}}$) would be equal to $[\text{Ca}]_{\text{CMAS}}$. If Al of clinopyroxene would enter solely as additional CaTs, one would expect to see an increased Ca-content of clinopyroxene at a given condition relative to the CMS system. Vice versa a decrease in Ca relative to the CMS system would indicate a preferential incorporation of MgTs. It appears that orthopyroxene behaves quite regularly with a more or less monotonous decrease in Ca for increasing

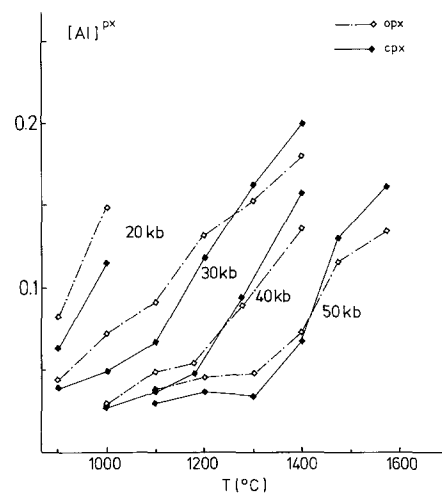


Fig. 3. Solubility of Al (cations per 6 oxygen) in ortho- and clinopyroxene vs. temperature in the system CMAS at 20, 30, 40 and 50 kb. Data from Perkins and Newton (1980) and this work

amounts of Al, which may be related to an added MgTs component either at the expense of the di component or as a simple dilution. Only at high T -high P conditions ($>1,400^\circ\text{C}$, >40 kb) there is an indication for a different behaviour. Clinopyroxene on the other hand shows a regular but complex behaviour. At low temperatures Ca in excess of the content of CMS pyroxenes is present, which could be described together with the Ca increase of orthopyroxene as a decreased mutual solubility of the pyroxenes (Perkins and Newton 1980). However, at higher temperatures this turns into a negative Ca^{xs} (relative to CMS) of clinopyroxene. The turning point is not at a constant value but shifts with increasing pressure to higher temperatures. It is inferred that this reflects a change in either the relative partitioning of CaTs:MgTs of ordered clinopyroxenes or a change in activities of these components with P, T . Within the context of an ordered model for clinopyroxene it is thus insufficient to calculate only non-ideality parameters for the influence of both MgTs and CaTs on the mixing properties of the enstatite component. A model based on ordered clinopyroxene would have to present a model for the partitioning between CaTs and MgTs on top.

This behaviour is also reflected in the solubility of Al in clinopyroxene. Figure 3 shows the data on the solubility of Al in both pyroxenes at different pressures and temperatures of Perkins and Newton (1980) and this work. The pattern shown in Fig. 3 may be interpreted as a strong curvature of the solubility of Al with temperature, differing between ortho- and clinopyroxene and changing with pressure. The difference in curvature between ortho- and clinopyroxene results for a given pressure in a point in the $T-X$ diagram where both pyroxenes dissolve equal amounts of Al. This point in terms of P and T coincides roughly with the turn from negative to positive " Ca^{xs} " in Fig. 2. However, alternatively the variation of Al in orthopyroxene with temperature at a fixed pressure may be approximated by straight lines except at 1,100 and 1,200°C and 50 kb. The variation of Al in clinopyroxene with temperature at a given pressure appears then to consist of two parts, both of which are approximately straight-lined variations, but having very different slopes. The intersection of the different slopes may

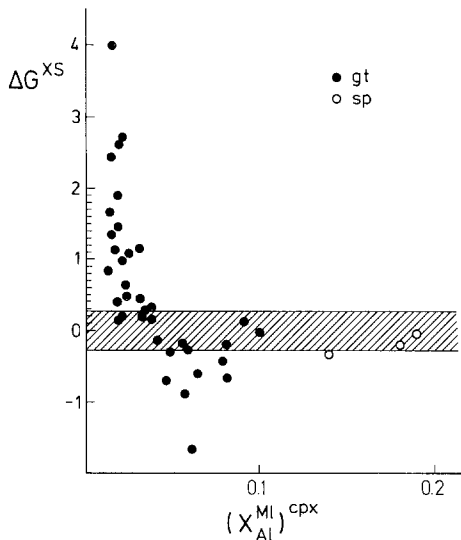


Fig. 4. The ΔG^{xs} (kJ) for reaction (A) calculated according to the model of Nickel and Brey (1984a), using experimental data in CMAS (Table 2) vs. the Al in the M1 site of clinopyroxene

be inferred to be related to a certain Al concentration (app. 0.04–0.06 formula units, equivalent to about 1 wt% Al_2O_3).

A further evaluation of this problem is obtained by the comparison of the experimental data in the system CMAS with thermodynamic models for the simple system CMS. Nickel and Brey (1984a) have shown that a model assuming two independent regular solutions for clino- and orthopyroxene is consistent with all reversed experimental data in CMS at pressures to 60 kb. The condition for equilibrium is $\Delta G_{P,T} = 0$, which for the model of Nickel and Brey (1984a) may be calculated as

$$\begin{aligned} \Delta G_{P,T} = & RT \ln K_D(A) \\ & + (W_H - TW_s + PW_v)^{\text{cpx}} (X_{\text{di}}^{\text{cpx}})^2 - W_{\text{opx}} (X_{\text{di}}^{\text{opx}})^2 \\ & + \Delta H - TAS + PAV. \end{aligned}$$

If a change in the mixing properties of the pyroxenes is due to the simple incorporation of Al into the pyroxene structure by a single, identical process, one would expect the deviation from $\Delta G_{P,T} = 0$ (or the amount of G^{xs}) to be a function of the concentration of Al in the pyroxene. This function may vary with P and T as an expression of ‘excess entropy’ or ‘excess volume’, but would have to be constrained by the condition $\Delta G^{\text{xs}} = 0$ for $X_{\text{Al}}^{\text{px}} = 0$. Thus we have plotted ΔG^{xs} versus the concentration of Al in the M1 site of clinopyroxene (defined as Al/2, Fig. 4). Shown as a shaded area in Fig. 4 is also the standard deviation of $\Delta G_{P,T}$ of reaction (A) from the equilibrium condition $\Delta G_{P,T} = 0$, using the thermodynamic formulation of Nickel and Brey (1984a) and the CMS data quoted therein. At Al-concentrations > 0.06 (i.e. $\text{Al}^{\text{M1}} > 0.03$) most of the data are within the uncertainty of the model of Nickel and Brey (1984a), including those with high Al-concentrations, coexisting with spinel (Fujii 1977). This suggests either ideal mixing or perfect balancing of all non-idealities due to Al in ortho- and clinopyroxene respectively. At Al-concentrations < 0.06 we however find large positive values for $\Delta G_{P,T}(A)$ (i.e. a positive ΔG^{xs}). Clearly it requires an extremely complex mathematical function to satisfy the condition $\Delta G^{\text{xs}} = 0$ for $X_{\text{Al}}^{\text{cpx}} = 0$ (see discussion below). The appar-

ent disagreement with this constraint at low Al concentrations thus supports the idea that at these low concentrations Al may enter clinopyroxene by a mechanism other than at high concentrations. It may be inferred that low Al leads to defects in the pyroxene structure, distorting its mixing properties.

Six experiments with intermediate Al-contents give negative $\Delta G^{\text{xs}}(A)$ values outside the standard error of the model of Nickel and Brey (1984a). The runs concerned are 1,300° C at 30 kb, 1,175 and 1,275° C at 40 kb, 1,470° C at 50 kb of this work and 900° C, 15 kb and 1,000° C, 20 kb of Perkins and Newton (1980). The negative ΔG^{xs} may be attributed to non-stoichiometry. Pyroxenes from runs with positive G^{xs} are within error stoichiometric. Calculating the mole fraction of Al in the M1 site of clinopyroxene as $\text{Al}/2$ gives for our four samples systematically higher values than 2-Si with typical differences in the order of $[(\text{Al}/2) - (2\text{-Si})] = 0.015$. We have checked the calibration of the microprobe with more than 20 international standards, including low- and high-Al clinopyroxenes, confirming that the effect seen is outside the statistical error of analysis. The two largest negative ΔG^{xs} values were calculated using data from Perkins and Newton (1980). Unfortunately we can not evaluate the published results of the other studies quoted in Table 2 in respect to non-stoichiometry, because they are either given as figures (Fujii 1977), partial analyses (Yamada and Takahashi 1984) or were probably recalculated on the basis of perfect stoichiometry (Perkins and Newton 1980). A P, T, X dependence of the non-stoichiometry is indicated from our results, but could not be resolved with the limited number of data available.

Whether this non-stoichiometry is due to reaction kinetics and hence only an experimental problem or is an expression of actual pyroxene behaviour relevant to natural rocks at those conditions is difficult to evaluate. We have calculated $(X_{\text{Al}}^{\text{M1}})^{\text{cpx}}$ from analyses of natural clinopyroxenes from garnet lherzolite as $(\text{Al} - \text{Cr} - 2\text{Ti} + \text{Na})/2$ and compared this to $[\text{Al} - (2\text{-Si})]$. The latter is then systematically higher than the former and the difference is in the order of the differences of the experiments quoted. However, some of this difference is probably due to the presence of an acmite component in natural clinopyroxenes.

Thus we can not evaluate the question of non-stoichiometry fully at this stage, but from Figs. 3 and 4 it is apparent that the concentration of Al has a much more severe effect than non-stoichiometry. Al can be considered as a trace element at low concentrations and may then behave according to Henry’s law. At high concentrations it may approximate Raoult’s law and intermediate Al-concentrations may correspond to a transitional stage, in which either reaction kinetics cause experiment-related problems or structural defects are systematically developed in pyroxenes.

Even when neglecting problems of non-stoichiometry thermodynamic treatment would have to consider non-ideal interaction for Mg–Al and ask for P, T dependent Margules parameters different for both pyroxenes. Further non-ideality may be caused by (P, T dependent) reciprocal or cross-site interaction (reaction (B)), the influence of which again may be different for both pyroxenes. We have tried out such a modeling procedure which involves a large number of fitting parameters compared to relatively few experiments. Indeed it is possible to obtain a near-perfect reproduction of experimental data. However, an evaluation showed these fitted coefficients to be statistically mean-

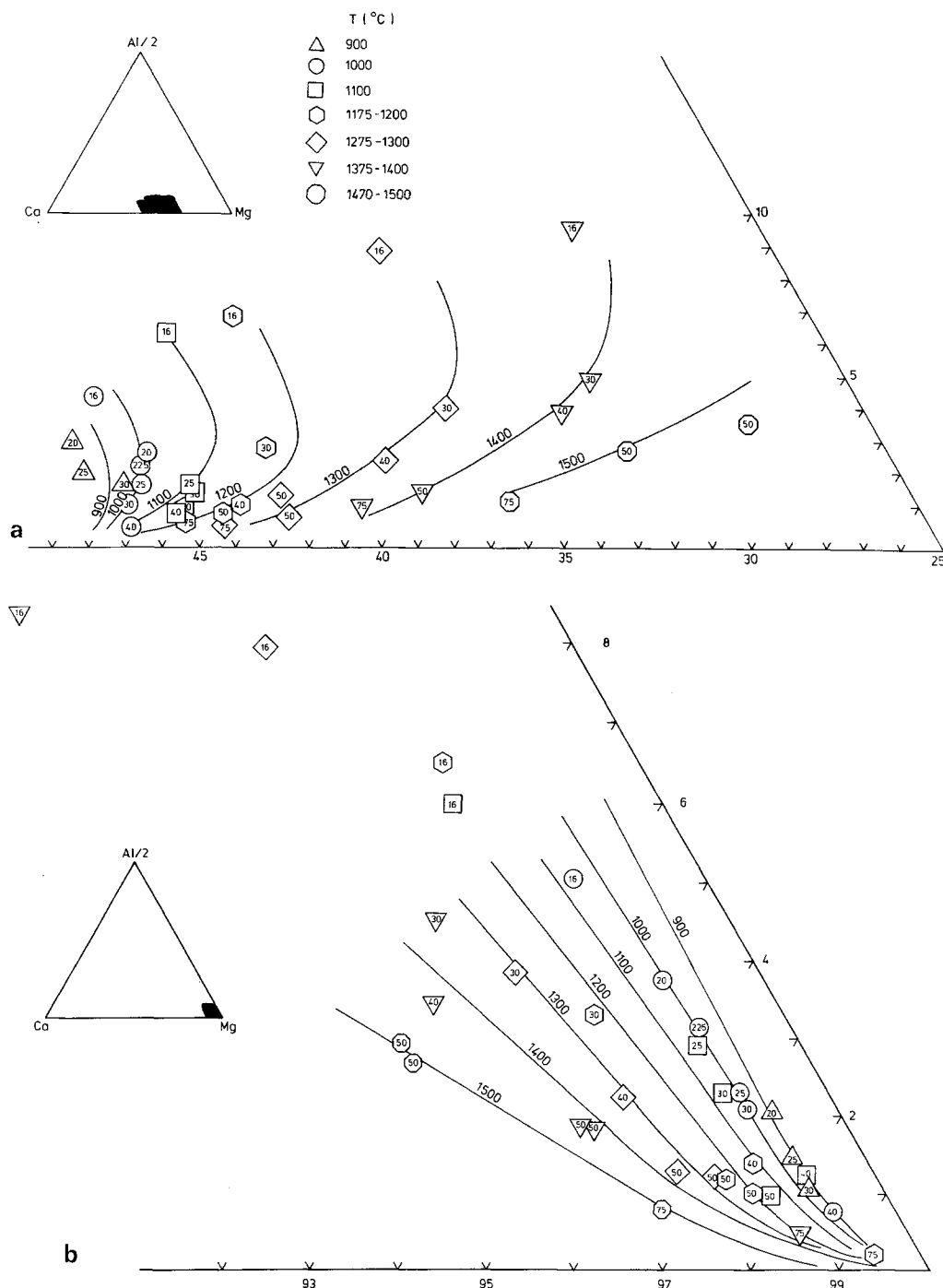


Fig. 5a, b. Projection of the composition of clino- (a) and orthopyroxene (b) from experiments in CMAS from SiO₂ onto the CaO-MgO-Al₂O₃-plane. Numbers within symbols denote pressure in kb. Isothermal lines are fitted by hand

ingless. Errors of estimate in the order of 100 to 200% of the fitted value were obtained and tests showed an even greater spread when only a single data set was left out from the fitting procedure. Thermometric formulations based on these highly complex models give therefore little physical information, but tend to make a thermometer highly dependent on the accuracy of analyses of small quantities of elements.

Thus at this stage we are not able to give a quantitative thermodynamic model of pyroxene behaviour in the system CMAS. Nonetheless the regularities exhibited in the experi-

mental results allow to evaluate pyroxene behaviour in an empirical way. In Fig. 5 we have plotted the data for ortho- and clinopyroxenes from SiO₂ of a CMAS tetrahedron onto the CaO-MgO-Al₂O₃ plane and fitted isothermal lines by hand. The difference between ortho- and clinopyroxene is quite pronounced. Similarly isobaric lines are shown in a plot of 1-Ca vs. X_{Al}^{M1} of clinopyroxene (Fig. 6). Translating the fits for clinopyroxene into a P, T field we can draw isopleths of $(X_{Al}^{M1})^{cpx}$ and " X_{en}^{di} " (Fig. 7). The latter is calculated as 1-Ca, i.e. correcting for Al as being present as CaTs. The problem of this formulation has been discussed

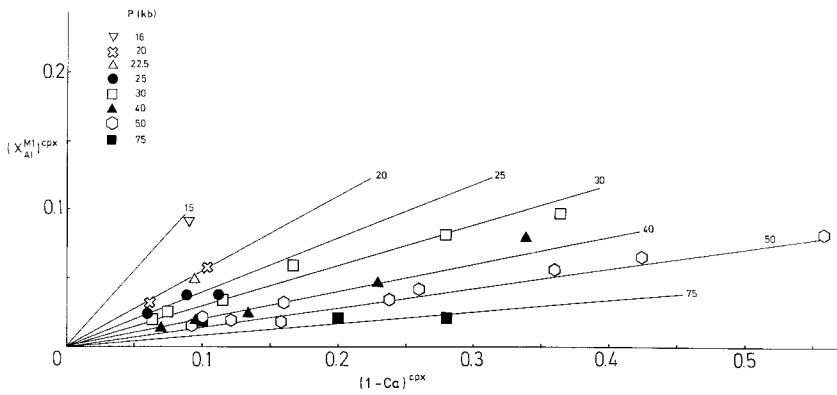


Fig. 6. $(1-Ca)$ of clinopyroxene vs. the mole fraction of Al in the M1 site at different pressures in the system CMAS. Data from Table 2. Isobaric lines are fitted by hand

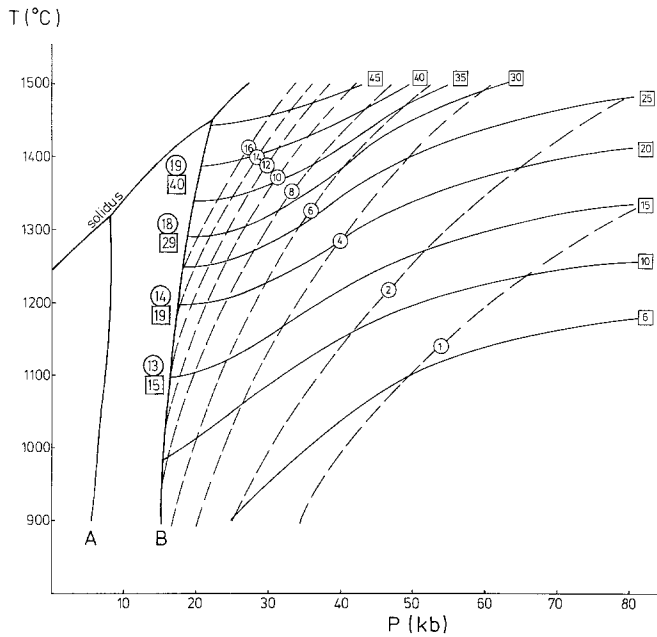


Fig. 7. Isopleths of $100 * X_{Al}^{M1}$ (dashed lines, circles) and $100 * X_{en}^{di}$ (calculated as $100 * (1-Ca)$, solid lines, squares) for clinopyroxenes in the system CMAS in a P, T field. Isopleths are translated from isothermal and isobaric fits in Figs. 5a and 6. Solidus, line "A" (plagioclase/spinel transition) and "B" (spinel/garnet transition) for CMAS are from Gasparik (1984). Values inside the spinel stability field are experimental results of Fujii (1976)

above. In Fig. 7 we demonstrate that such " X_{en}^{di} " - isopleths have a complex shape and are strongly pressure dependent even at low T , low P conditions, contrasting the near - P independence of X_{en}^{di} -isopleths at low T in the system CMS (Nickel and Brey 1984a). Al-isopleths are strongly curved in P, T .

Despite problems with thermodynamic analyses of pyroxene behaviour it is possible to derive empirical thermometric expressions. Empirical thermometry relies on the fact that for exchange reactions many non-idealities of mineral behaviour cancel each other. Thus one has to find a suitable expression that utilizes this effect best. Empirical geometers are however confined to be used only within a calibrated range of P, T, X conditions. Evans and Trommsdorff (1978) and Ehrenberg (1982) demonstrated that previous empirical two-pyroxene thermometry in a widely used form (Wells 1977) shows systematic errors with temperature when applied to CMS data. Nickel and Brey (1984) demonstrated that the lack of a pressure correction in this thermometer results in the characteristic pattern of T -overestimation at low and high temperatures, T -underestimation at medium temperatures combined with a shift of this "V"-shape to give lower estimates at higher pressures (Fig. 3a of Nickel and Brey 1984a). This pattern is demonstrated in the system CMAS as well (Fig. 8c). Data from extreme conditions (up to 100 kb) expose the problem extremely.

The CMS data used for calibration purposes by Wells (1977) were those of Davis and Boyd (1966), Boyd and Schairer (1964), Kushiro (1972), Mori and Green (1975,

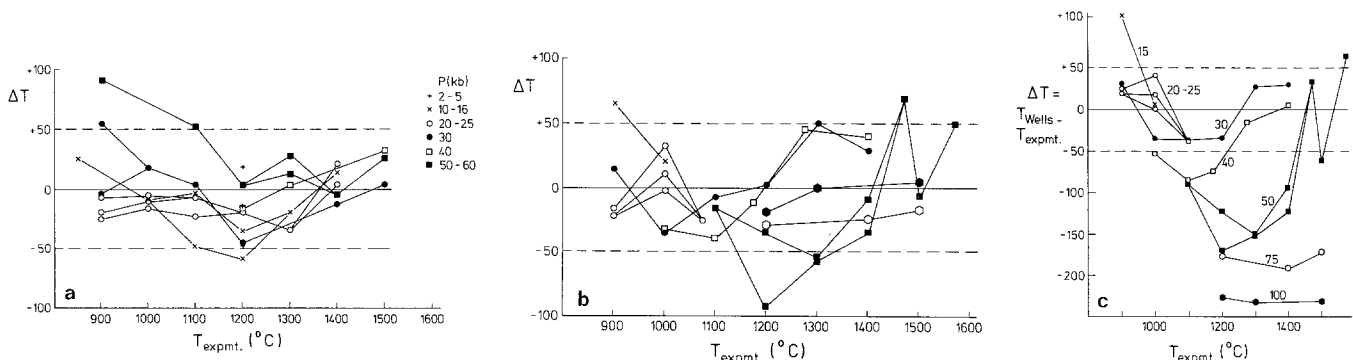


Fig. 8a-c. Plots of error of estimate ($\Delta T = T_{estimate} - T_{experiment}$) vs. the experimental temperature. Data sources see Table 1 of Nickel and Brey (1984a) and Table 2 of this work. Shown are the application of equation (1) of this work to experiments in CMS (Fig. 8a) and CMAS (Fig. 8b) and the application of the Wells (1977) thermometer to CMAS (Fig. 8c)

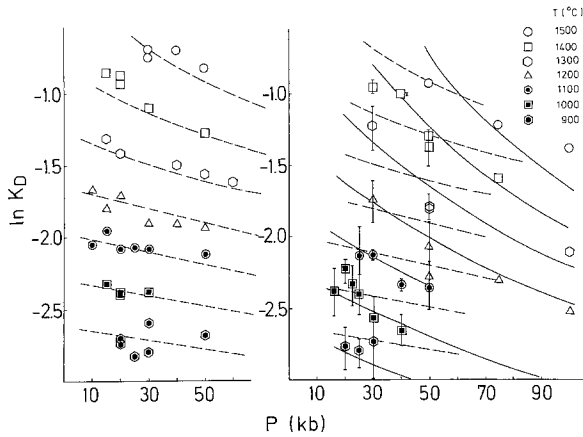


Fig. 9a, b. Pressure dependence of the $\ln K_D$ of reaction (A) at various temperatures in the systems CMS (a) and CMAS (b). Data sources: see Table 1 of Nickel and Brey (1984a) and Table 2, this work. Isothermal lines (dashed lines=CMS, solid lines=CMAS) are regressed individually for the CMS and CMAS system using a simple fit of the type $1/T = a + b * (\ln K_D)^2 + c * P$. Regression lines from a are drawn into b for comparison. Note that the crossover of the regressed isotherms coincide in P, T roughly with the crossover of Al-solubility of the pyroxenes shown in Fig. 2

1976), Lindsley and Dixon (1976), Nehru and Wyllie (1974) and Warner and Luth (1974), in CMAS only data from Cawthorn (1976), Akella (1976) and Boyd (1970) were available. Ehrenberg (1982, Fig. 11) showed earlier that for these data a plot of the type $\ln K_D$ vs. $1/T$ (as used to calibrate the Wells (1977) thermometer) does not yield a straight-line relationship, but shows rather a curved path, which Ehrenberg (1982) fitted to a quadratic equation. Using more recent data (see Table 1 of Nickel and Brey 1984a) confirms the non-linearity of the correlation between $1/T$ and the $\ln K_D$. The shape of this correlation is similar to a function $y=f(1/x)$. Thus we have fitted the $\ln K_D$ directly with T instead of $1/T$ and circumvented in this way many complications of empirical two-pyroxene thermometry. Thermodynamic formalisms are often useful even for empirical modeling, but empirical models are not constrained by and thus not confined to thermodynamic formalisms. We demonstrate here the we believe simplest formulation possible to reproduce experimental conditions reasonably well.

The $\ln K_D$ is also dependent on P . The difference in the pressure dependence of “ X_{en}^{di} ” of clinopyroxene between CMS and CMAS is not completely balanced by a difference in orthopyroxene. Thus there is a different P -dependency of the $\ln K_D$ between the systems (Fig. 9) and a very simple fit for both systems is bound to show systematic errors. A multiple regression (correl. coeff. $r=0.99$) for the dependency of T on $\ln K_D$ and P for CMS and CMAS yielded the formula

$$T(^{\circ}\text{C}) = 1616.67 (\pm 14.7) + 287.935 (\pm 5.5) * \ln K_D + 2.933 (\pm 0.25) * P(\text{kb}) \quad (1)$$

where

$$K_D = ((1-\text{Al}/2) * (1-\text{Ca})^{\text{opx}}) / ((1-\text{Al}/2) * (1-\text{Ca})^{\text{px}}) \quad (d)$$

Figure 8a and b show the expected result, where CMS data at 50 kb and 900 and 1,100°C indicate systematic overestimation. However, almost all of the data, covering a very wide P, T range in both CMS and CMAS are repro-

duced within $\pm 50^{\circ}$ and hence close to an estimated error of $\pm 20\text{--}30^{\circ}$ attributed to the combined uncertainty of experimental and analytical procedures. Thus even very complicated and elaborate models will not give much of extra accuracy in terms of data reproduction. Very simple empirical thermometers may therefore be used or developed in order to estimate conditions of origin of rocks. However, these thermometers must be calibrated from experiments in chemical systems very close to the composition of the rocks concerned. The formulation above is only valid for CMS and CMAS in the P, T range specified by the experiments and should not be applied to natural rocks. The work in order to develop or evaluate empirical geothermometers in complex systems is in progress (Nickel and Brey 1984b and in prep.).

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