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Reassessment of the garnet-clinopyroxene Fe-Mg exchange thermometer: I. Evaluation of the Pattison and Newton (1989) experiments

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Abstract This is Part I of a two-part study on the garnet(Grt)-clinopyroxene(Cpx) Fe-Mg exchange equilibrium widely used in geothermometry of amphibolites, granulites and eclogites. The experimental data set previously published by Pattison and Newton (PN) on this equilibrium comprises potentially the largest source of data used for extraction of thermodynamic properties for Grt and Cpx and for formulation of a new thermometer expression (Part 2 of this study). However, the experiments suggested unusual Grt and Cpx solution properties and resulted in a geothermometer expression that generally returns low temperatures for granulites. To verify the reliability of the experiments, and to test the experimental technique of Grt buffering used in the PN study, 69 of the 125 PN runs were reanalysed using wavelength dispersive spectroscopic analysis guided by backscattered electron images. Special attention was given to analysis of compositional changes in Grt in addition to Cpx. With minor exceptions, the reanalysis supports the analytical results of the original PN study. The mechanism of equilibration in the runs was a multicomponent solution-precipitation process involving dissolution of metastable Grt and Cpx starting materials and precipitation of newly formed Cpx and Grt, the latter assumed to represent equilibrium compositions. The experiments cannot be regarded either as reversed or as strictly bracketing. Nevertheless, Cpx compositional parameters, including Mg#, Na, Ca and Al, show the same smooth variations with temperature, pressure and composition as found by PN, suggestive of a close

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approach to equilibrium. Grt in run products retained the moderate heterogeneity of the starting Grt, although there are subtle compositional trends indicating small changes in Grt Mg# consistent with mass balance constraints. These results uphold the essential validity of the technique of Grt buffering used in the experiments. Nevertheless, it is possible that the final Grt compositional may not coincide with the nominal starting Grt compositions, requiring assignment of compositional uncertainties to Grt for purposes of thermodynamic modelling of the data. Cpx analyses also require assignment of non-zero compositional uncertainties.

Introduction

This paper is Part 1 of a two-part study on the thermodynamics of garnet-clinopyroxene equilibria, focusing on the temperature-sensitive Fe-Mg exchange equilibrium widely used in geothermometry of amphibolites, granulites and eclogites. The purpose of Part 1 is twofold: to present the results of a detailed reanalysis of Pattison and Newton's (1989) large but controversial experimental data set on garnet-clinopyroxene Fe-Mg exchange (hereafter referred to as PN), and to assess the general validity of their experimental approach in which garnet buffering by overwhelming abundance was used to constrain the exchange isotherms. This technique, first introduced by Ferry and Spear (1978) in their study of garnet-biotite Fe-Mg exchange, has been used extensively in subsequent studies investigating Fe-Mg exchange between other mineral pairs (e.g. garnet-olivine, Hackler and Wood 1989; garnet-orthopyroxene, Eckert and Bohlen 1992; olivine-clinopyroxene, Perkins and Vielzeuf 1992). The reanalysed Pattison and Newton data form the largest component of the experimental data base used by Berman, Aranovich and Pattison (1994) in Part 2 to extract new

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thermodynamic data and activity-composition expressions for garnet and clinopyroxene end members, including formulation of a new thermometer expression.

The Pattison and Newton Experiments

Pattison and Newton (1989) investigated the T-P- X_{Mg} - X_{Ca} equilibrium conditions of the exchange reaction:

 $\begin{array}{ll} \text{(A)} & Mg_3\Lambda l_2Si_3O_{12} + 3CaFeSi_2O_6 = Fe_3Al_2Si_3O_{12} + 3CaMgSi_2O_6 \\ & \text{Pyrope} & \text{Hcdenbergite} & \text{Almandine} & \text{Diopside} \end{array}$

The two previous experimental calibrations of this equilibrium, Råheim and Green (1974) and Ellis and Green (1979), and a more recent experimental investigation by Green and Adam (1991), were based on synthesis experiments from glass starting materials. In order to minimize potential problems of formation of metastable compositions from rapid crystallization of glass, Pattison and Newton (1989) used crystalline starting materials and attempted to bracket the final compositions from Fe-rich and Mg-rich compositional directions, thereby increasing confidence that equilibrium compositions were obtained or closely approached in the experiments. The PN experiments also investigated the effect of Ca content and Mg# in garnet on the equilibrium more explicitly than the previous studies. The P-T range of most of the PN experiments was 800-1200° C and 15-29 kbar. The large number of experiments they performed (125), in addition to many repeat runs to demonstrate reproducibility of the experimental results, yielded a substantial experimental data base showing smooth compositional variations as a function of P, T and composition, from which they calibrated a semi-empirical thermometer expression.

PN found that $\ln K_D = (Fe/Mg)Grt/(Fe/Mg)Cpx$ depended not only on temperature and grossular content of garnet, but also on Mg # (= Mg/(Mg + Fe)) of garnet. Their results have been controversial from two points of view. First, they found an unusual pattern of lnK_D vs Mg# (Fig. 10, PN), which suggested strong non-ideality on the Fe-Mg joins in either or both of garnet and clinopyroxene, a result which seemed to contradict inferences from other Fe-Mg exchanges involving one or other of the two minerals (e.g. garnet-orthopyroxene, Lee and Ganguly 1988; garnet-olivine, Hackler and Wood 1989; olivine-clinopyroxene, Perkins and Vielzeuf 1992). Second, their thermometer expression returns low temperature estimates for many garnet-clinopyroxene amphibolites and granulites (Table 6, PN), many of which are too low as peak metamorphic temperatures to be plausible from phase equilibrium constraints. The lowest and most puzzling temperature estimates are obtained from Fe-rich compositions, the compositional region of greatest uncertainty in PN's study. This has resulted in many workers dismissing the PN calibration in favour of the older Ellis and Green (1979) calibration, which, despite some experimental shortcomings and a poorly defined pressure effect, returns granulite temperature estimates which agree better with what are viewed as "reasonable" peak temperature conditions. The danger in this reasoning is that it assumes that there is little to no down-temperature Fe-Mg resetting as rocks cool from peak temperature conditions, an assumption which has been challenged by Frost and Chacko (1989) among many others, and has been demonstrated to be invalid in the pelitic granulites studied by Pattison and Bégin (1994).

Because of the controversial aspects of the PN study, several workers (e.g. E.J. Essene, personal communication to DRMP 1991; Perkins and Vielzeuf 1992) have suggested possible problems in the PN experiments. These include:

(1) imprecise and possibly inaccurate mineral analyses due to use of energy dispersive (EDS) rather than wavelength dispersive (WDS) spectroscopic analysis of their starting materials and run products, especially for the light atomic mass elements Na and Mg,

(2) failure to use back-scattered electron (BSE) images to guide analysis of run products, and to provide information on reaction mechanism and extent of reaction,

(3) non-negligible Fe^{3+} contents in Cpx following the runs,

(4) uncertain effects on K_D of variable Na, Ca and Al contents of Cpx, which were not constrained in the experiments,

(5) heterogeneous garnet compositions, and

(6) possible temperature variations due to "poisoning" of the chromel-alumel and tungsten-rhenium thermocouples by silver from the sample containers used in the experiments.

Many of these types of possible shortcomings, in addition to several others not listed above, also apply to other experimental studies. To assess these concerns in the PN data, 69 of the 125 PN runs were reanalysed employing a combination of BSE imaging and WDS analysis. In addition, a more concerted attempt was made to gauge reasonable levels of analytical uncertainty on the experimental compositions for the purposes of thermodynamic data extraction in Part 2 of this study.

Technique of garnet buffering in Fe-Mg exchange studies

The technique used by PN to obtain apparent brackets of clinopyroxene compositions in equilibrium with garnets of fixed Ca content and Mg# is based on the concept of garnet buffering, first used by Ferry and Spear (1978) in their study of garnet-biotite Fe-Mg exchange. The technique involves the insertion of an overwhelming abundance of garnet relative to the other exchanging phase (e.g. Grt:Bt = 98:2 in Ferry and Spear; Grt:Cpx = 95:5 and 90:10 in PN), thereby effectively fixing the bulk composition of the experimental system close to that of the garnet (see Fig. 2 of Ferry and Spear 1978 and Fig. 1 of PN). From mass balance constraints, this dictates that significant compositional change can occur in the mineral in small modal abundance (e.g. biotite in Ferry and Spear; clinopyroxene in PN) without significant compositional change in the garnet, thereby allowing the determination of the composition of the coexisting phase (e.g. biotite or clinopyroxene) for a known garnet composition.

Pattison and Newton (1989) examined compositional changes in garnets in a few of their experiments. They found small but generally consistent changes in garnet rim compositions consistent with mass balance constraints, supportive of the assumption of effective garnet buffering. In the reanalysis reported in this study, a more detailed examination of garnet compositional variation in the PN experiments was made as a critical test of the garnet buffering technique.

Analytical procedures

The same polished mounts of run products as in PN were reanalysed using WDS analysis. Approximately one third of the runs were analyzed on an ARL-SEMQ electron microprobe in the Department of Geology and Geophysics, University of Calgary (UC), and the remainder on a Cameca SX-50 microprobe at the Geological Survey of Canada (GSC) in Ottawa. BSE images were used to guide the reanalysis on both instruments. For the UC instrument, the operating conditions, data reduction scheme and typical detection limits and analytical precision for Na, Ca, Fc, Mg, Al and Si are the same as those listed in Nicholls and Stout (1988). Well characterized natural and synthetic minerals close in composition to those of the unknowns were used as standards: for clinopyroxene, natural ferrosalite was used for Fe, Si and Ca and synthetic diopside-jadeite was used for Na, Mg and Al; for garnet, natural almandine was used Fe and Si, and an intermediate-composition natural garnet was used for Ca, Mg and Al (Na was also analysed for, but none was detected). These standards resulted in excellent stoichiometry for both minerals. For the GSC instrument, operating voltage was 15 kV with a beam current of 10 to 30 nA. Counting time varied from 10-20s, depending on the element and beam current. The diameter of the excitation volume for the operating conditions used corresponds to about 2-4 µm depending on the element (equations on pp 200-201 of Reed 1993). Data reduction followed the routine of Pouchou and Pichoir (1984), using oxide standards.

To check for possible systematic differences between the two microprobes and different types of standards used, eleven experimental run products were analysed on both instruments. The mean and range of analyses for both garnet and clinopyroxene in all eleven experiments showed excellent agreement (e.g. for Mg#, agreement to within 0.01), indicating that no complexities in interpretation were introduced by the use of different instruments.

Garnet and clinopyroxene formulae were normalized to 12 and 6 oxygen atoms, respectively, and ferric iron in clinopyroxene was inferred from stoichiometry according to the scheme of Lindsley (1983). The analytical uncertainties on both the UC and GSC microprobes are about 2% of the amount present for CaO, FcO, MgO, Al₂O₃ and SiO₂, and 5% for Na₂O. For calculated Mg#, the propagated uncertainty (2 sigma) is $\pm 0.007 - 0.01$.

Compositional scans across individual garnet and clinopyroxene grains were made using the automated Cameca SX-50 microprobe (GSC). The spot analyses were collected every $1.5-2.0 \mu m$, depending on the grain size, with the starting and final points of profiles chosen about 2 μm from the edge of the grains to minimize edge effects (Ganguly et al. 1988).

Individual analyses were accepted if elemental oxide totals were 100 \pm 2% and stoichiometries did not deviate by more than 1.5% in any cation site from ideal garnet or elinopyroxene mineral formulae. With these criteria applied, Fe³⁺/Fe_{total} in the reanalysed clinopyroxenes was less than 0.02, an amount most likely related to the analytical uncertainties. Good agreement between the tschermak component in Cpx calculated using two different schemes (2-Si and (Al_{total}-Na)/2) provided an additional criterion to indicate the high quality of the accepted analyses.

Run textures

Typical textures for the run products are shown in BSE images in Fig. 1. Figs. 1a and 1b show run products for Mg-rich (Di_{90}) and Fe-rich (Di_{50}) starting clinopyroxenes in 800 and 900° C runs, respectively, whereas Figs. 1c and 1d show run products for Di_{90} and Di₅₀ starting clinopyroxene in 1200° C runs. In the 700-1000° C runs, 10% by mass of oxalic acid hydrate was added to a loose mixture of garnet and clinopyroxene crystals. During the experimental runs, the oxalic acid hydrate broke down to graphite and a CO₂-H₂O vapour, the latter of which fluxed the experiments. In the 1100 and 1200 °C runs, although no flux was added to the charges, the charges emerged as cemented pellets. BSE images reveal that in some runs a small amount of what appears to be intergranular melt was generated, which probably acted as a flux. The source of the melt is enigmatic, but it may have been produced from reaction of residual, tenaciously adsorbed moisture in the starting mineral mix, and/or from possible penetration of material from the pressure medium into the experimental charges.

In Fig. 1a, the grain size of garnet (lighter coloured grains) is generally smaller than that of clinopyroxene (darker coloured grains), noting the abundance of fine grained garnet fragments in addition to the more obvious larger grains. Smaller grain size of garnet compared to clinopyroxene is typical for all the runs in the PN study. The sharp edges of the inserted garnet fragments have been rounded off, suggestive of dissolution. The Di₉₀ clinopyroxene seeds are subhedral and preserve their crystal form, but show evidence of rounding at the edges, indicative of partial dissolution. Compared to the relatively dark, Mg-rich cores (Mg # = 0.9), there is a subtle lightening at the rims indicative of Fe enrichment, consistent with measured compositions (Mg# of rims = 0.77). In Fig. 1b, the Di_{50} starting clinopyroxene is markedly corroded, suggestive of



Fig. 1 Backscattered electron images of run products. a Run 3a: 15 kbar, 800° C, 358 h; starting Cpx-Di₉₀; starting Grt- $X_{Ca} = 0.3$, Mg # = 0.29. The dark coloured grains with the light rims are clinopyroxene grains (starting Mg # = 0.9), whereas the light coloured grains and aggregates are garnet. The lightening seen at the rims of the clinopyroxene grains corresponds to compositional changes (Table 1) including Al- and Fe-enrichment (Mg # = 0.7), whereas the lightening at the rims of some garnets is a spurious edge effect (see text). b Run 32b: 15 kbar, 900° C, 142 h; starting Cpx-Di₅₀; starting Grt- $X_{ca} = 0.3$, Mg # = 0.57. The prominent corroded grain with the light coloured central portions is clinopyroxene (starting Mg # = 0.5), showing darkening along its rims and in patches subparallel to the cleavage. These zones correspond to compositional changes (Table 1) including Al- and Mg-enrichment (Mg # = 0.8). The rest of the grains are garnet, some of which show an apparent lightening at their rims which is an edge effect (see text). c Run 70d: 15 kbar, 1200° C, 24 h; starting Cpx-Di₉₀; starting Grt- $X_{Ca} = 0.2$, Mg # = 0.29. The light coloured grains are garnet whereas the dark areas are clinopyroxene. In the large central clinopyroxene, note the curious pattern of dark cores surrounded by a network of lighter coloured material. The dark cores are unreacted Al-free starting $Cpx(Mg \neq = 0.9)$, whereas the network consists of recrystallized Albearing Cpx showing Fe-enrichment (Mg# = 0.55) (see text for discussion). d Run 70c: 15 kbar, 1200° C, 24 h; starting Cpx-Di₅₀; starting Grt- $X_{Ca} = 0.2$, Mg # = 0.43. The large central area is a clinopyroxene grain, surrounded by numerous small garnet grains showing rounding at their edges. In the large area of clinopyroxene, there is a light-coloured core of unreacted Al-free starting Cpx(Mg # = 0.5), surrounded by a recrystallized zone of Al-bearing, Mg-enriched Cpx(Mg # = 0.63). The bright spots in the clinopyroxene core are Fe blebs, most likely residual from clinopyroxene synthesis

significant dissolution. Darker coloured (Mg-richer) zones of equilibration occur both along the rims and along what are most likely cleavage planes. The rims and equilibrated zones have an Mg# of 0.80 compared to an Mg# of 0.5 in the unreacted portions of the grain. Overall, the degree of dissolution and of reaction of the Fe-richer Di₅₀ starting clinopyroxene appears to be greater than for the Mg-richer Di₉₀ composition. In all of the Fig. 1 photographs, there is an apparent lightening at the margins of garnet which is a spurious edge effect from BSE imaging which does not correspond to any significant compositional change.

In Figs. 1c and 1d, both the garnet and clinopyroxene in the 1200° C runs show more rounding than in the lower temperature runs, indicative of more substantial dissolution. In Fig. 1c, the Di_{90} starting clinopyroxene shows a curious mosaic pattern of unreacted (dark) domains surrounded by a light coloured network of equilibrated, Fe-richer clinopyroxene. This pattern may be due to the plane of the polished section being roughly perpendicular to the *c*-axis of the clinopyroxene crystal, with the light coloured network possibly due to partial reaction along cleavage planes. In Fig. 1d, a relatively homogeneous Di_{50} seed shows evidence for substantial recrystallization at its margins,



GARNET COMPOSITIONS FROM EXPERIMENTAL

Fig. 2 Garnet compositions after experimental runs compared with starting compositions. The *solid dots and lines* represent the mean and absolute range of measurements. The *horizontal lines* are the limits of the range of the starting compositions. The numbers adjacent to the starting ranges are the intended garnet compositions. The *dashed lines* show variation of Mg $\# = \pm 0.01$ around the intended starting compositions, corresponding to analytical uncertainity

resulting in a ca. 10 μ m-wide recrystallized, Mg-richer rim. The bright spots in Fig. 1d are small Fe-blebs found in some of the clinopyroxene starting materials, most likely residual from their synthesis.

The textures in Fig. 1 suggest that the equilibration mechanism in the experiments involved solutionprecipitation, rather than Fe-Mg diffusion as assumed by PN. In all runs, garnet shows evidence for rounding suggestive of dissolution, while Cpx in Fig. 1b shows obvious signs of corrosion. In Figs. 1b and 1c, the patchy zones of equilibration both at the rims and internal to the clinopyroxene grains are more easily explained by solution-precipitation than diffusional exchange alone. In Fig. 1d, the abrupt discontinuity



Fig. 3 Corc-to-rim step-scan profile across garnets from Run 85b: 15 kbar, 900° C, 376 h; starting Cpx-Di₂₀; starting Grt- $X_{Ca} = 0.2$; Mg# = 0.14. Note the irregular patterns within individual grains, and the variation in Mg# between the three separate grains. There is a suggestion of overall convergence of the rim compositions to a value of 0.135 \pm 0.01 (close to the nominal starting composition)

between relatively homogeneous, unreacted starting clinopyroxene in the centre of the grain and more turbid, recrystallized rim material that mantles the central unreacted portion is most consistent with a solution-precipitation mechanism.

Compositional zoning

Garnet

Garnet compositions after the runs generally showed the same heterogeneity (range of compositions) as the starting garnet (Fig. 2). Care was taken to analyse large and small garnets, and garnets close to and far from Cpx crystals. Individual core-rim profiles in garnets showed no consistent patterns, although overall rims of garnets after the runs showed a slightly narrower range of compositions than the starting garnet (Fig. 3). Based on averages of rim and core compositions in individual runs, there is a subtle but generally consistent pattern of garnet rims having become Mg-richer in runs in which Cpx became Fe-richer, and garnet rims having become Fe-richer in runs in which Cpx became Mgricher (Fig. 4). The magnitude of these shifts is generally $Mg \neq = 0.02$ or less. As shown in Table 2 of PN, these subtle changes in garnet composition are consistent with mass balance constraints in the runs, in which overwhelming garnet abundance dictates small compositional changes in garnet even for large Cpx compositional changes. Even with these slight compositional shifts, however, the mean and range of the rim

CHANGE IN COMPOSITION OF GARNET RIMS METHOD A



Fig. 4 Differences in average 100Mg# between rims and cores of garnet from Method A runs of PN(Grt:Cpx = 95:5). Solid dots represent the unreacted starting Grt compositions; arrowheads show the average difference between the rim compositions and the core compositions. Runs are grouped into pairs for which the starting garnet composition and run conditions were the same, but the starting Cpx compositions were different: in each pair, the left hand arrow is for garnets in runs in which Mg-rich starting Cpx became Fe-richer, and the right hand arrow is for garnets in runs in which Fe-rich starting Cpx became Mg-richer. Arrows with hooks indicate runs in which garnet rims apparently changed in Mg # in the same sense as the Cpx. The light solid horizontal lines represent an envelope of $100Mg \# = \pm 3$ about zero change; the dashed horizontal lines represent an envelope of $100Mg \# = \pm 1$, corresponding to analytical uncertainty. The pairs of runs shown ranged in temperature from 800 to 1200° C

compositions generally fall within the compositional range of the starting garnet.

Clinopyroxene

In contrast to the subtle compositional changes in garnet, clinopyroxene shows strong evidence of recrystallization (Fig. 1). Fig. 5 shows profiles of Mg#and Al cations for 6 oxygens across three individual Cpx grains for different experimental conditions. The profiles reveal a central core of Al-free starting clinopyroxene with Mg# within the measured homogeneity range of the synthesized material, mantled by a rim of Al-bearing clinopyroxene of a different Mg#. The significant variations in composition between core and rim demonstrates that

Fig. 5a–c Rim-to-rim step-scan profiles across clinopyroxene grains. See text for discussion. The *solid vertical lines* are the inferred location of the interface between Al-free seed material and Al-bearing rim material, whereas the *dashed lines* are the limits of convolution effects if the interface were discontinuous and abrupt (see text). A Run 76b(1): 15 kbar, 800° C, 484 h; starting Cpx-Di₉₀; starting GrI- $X_{ca} = 0.2$, Mg # = 0.43. B Run 88c: 15 kbar, 1200° C, 60 h; starting Cpx-Di₉₀; starting Grt- $X_{ca} = 0.25$, Mg # = 0.33. C Run 88d: 15 kbar, 1200° C, 60 h; starting Cpx-Di₅₀; starting Grt- $X_{ca} = 0.25$, Mg # = 0.33



intragranular diffusion was not rapid enough to homogenize the Cpx compositions, consistent with small expected diffusion penetration distances for experimental run times calculated by Pattison (1994).

Convolution effects (Ganguly et al. 1988) complicate the interpretation of the nature of the interface between the rim material and the core material. In Fig. 5, the solid lines represent the inferred location of the interface, located in the interval of steepest slope (Ganguly et al. 1988) of the Al profile, whereas the dashed lines on either side of the solid line represent the region in which the excitation volume from microprobe analysis (ca. 2.2 μ m radius; Pattison 1994) would incorporate material from both sides of the interface.

In Figs. 5b and 5c the slope of composition vs radial distance is generally steeper for Al than for Fe-Mg, supporting theoretical considerations (Dowty 1980; Anovitz 1991) and experimental data (Ghose and Ganguly 1982; Jaoul et al. 1991; Ganguly and Tazzoli 1994) indicating that Fe-Mg diffusion in Cpx is faster than Al diffusion. The volume of clinopyroxene that reacted in the runs varied with starting clinopyroxene composition and temperature. For the same starting Cpx (Di_{90}) , the extent of Fe-Mg diffusion into the cores of the Cpx seeds (defined by gradients in Mg # in Alabsent Cpx) is greater at higher temperatures than at lower temperatures, as expected (compared Figs. 5A and 5B). However, in the 800° C run there is no unambiguous diffusional gradient in Fe-Mg between core and rim that could be distinguished from convolution effects if the interface were abrupt; at 1200° C there is evidence for a diffusional gradient in Mg# 2-3 μ m inwards of the limits of convolution effects. Although the above estimate is only approximate, a diffusional penetration distance of 4-5 µm is in good agreement with calculated diffusion penetration distances (Pattison 1994) based on the orthopyroxene Fe-Mg diffusion data of Ganguly and Tazzoli (1994), estimated by Ganguly (in Ghose and Ganguly 1982) to be comparable to that for clinopyroxene.

For the same run conditions (1200° C) , Mg-rich starting Cpx (Di_{90}) was apparently less reactive than Fe-richer Cpx (Di_{50}) , as revealed by smoother core-rim compositional gradients in Di_{50} Cpx compared to the relatively abrupt core-rim gradients in Di_{90} Cpx (compare Figs. 5B and 5C). These observations suggest that rates of recrystallization and/or diffusion in Cpx may be faster in Fe-rich compositions than in Mg-rich compositions.

Reaction mechanism and implications for reversibility

In addition to the textural features noted above, compositional changes in Cpx argue for multicomponent solution-precipitation in the experiments: inserted Naand Al-free starting clinopyroxene seeds took on Na and Al and became less Ca-rich during the runs. The only source for exchange of Ca and Al was the garnet, whereas the Na was likely introduced as a contaminant into the experimental charges (see discussion below, under assessment of problems section).

Diffusion calculations in Pattison (1994) support a dissolution-precipitation mechanism by showing that for the temperatures and run times involved, the calculated diffusion penetration distance of Fe-Mg volume diffusion in clinopyroxene is on the order of a few microns except for runs above 1000° C. It would therefore be unlikely by Fe-Mg diffusion alone to produce a rim wide enough to analyse on the electron microprobe without incorporating a substantial proportion of unreacted starting composition. The close agreement between pairs of runs involving Fe-rich and Mg-rich starting Cpx at the same run conditions indicates the growth of rims wide enough that the microprobe excitation volume (diameter ca. 4.4 µm, Pattison 1994) did not overlap with the unreacted seed material. Rims and equilibrated zones in Cpx from even the lowest temperature runs (800° C) range up to 6 μ m width, and increase with temperature (see Figs. 1 and 5).

Evidence for participation of *both* garnet and clinopyroxene in the solution-precipitation process is provided by the subtle but generally consistent changes in garnet rim compositions depending on whether the Cpx became Mg- or Fe-richer. Therefore, in contrast to an Fe-Mg diffusion couple being established between inserted garnet and Cpx crystals in the runs, as was assumed by PN, probably the only place where intragranular diffusion by itself effected detectable compositional gradients appears to have been between the newly precipitated rims and the unreacted seed material in the 1200° C and possibly 1100° C runs.

The above considerations mean that pairs of experiments involving initially Fe-rich and Mg-rich starting clinopyroxene compositions cannot be treated either as reversals or as strictly limiting compositional brackets (Pattison 1994). First, there would be no way to return the newly precipitated, sub-calcic, Na- and Al-bearing clinopyroxene compositions back to the Na- and Alfree, Ca-saturated starting clinopyroxene compositions by changing P or T, which violates the criterion of reversibility. Second, the clinopyroxene changed in several compositional parameters rather than just Fe-Mg, meaning that the final compositions are not bracketed for all components (e.g. the Al-content of the product clinopyroxene was only approached from the Al-free direction and the Ca-content of the subcalcic product clinopyroxene was only approached from the Ca-rich direction). Third, in contrast to a continuous diffusionally-controlled compositional gradient from unreacted starting Cpx to equilibrated rims, which unambiguously establishes the direction to equilibrium, the inferred solution-precipitation mechanism opens

the possibility of kinetically controlled 'jumps' to the final rim compositions, from which direction to equilibrium may be ambiguous (Pattison 1994). This last point violates the criterion of bracketing, which requires unambiguous knowledge of the direction to equilibrium. This process may additionally account for some of the compositional overlaps observed in the PN experiments.

Despite these considerations, a close approach to equilibrium in the runs is suggested by the smooth variations in Mg#, Ca, Na and Al content in Cpx with temperature, pressure and composition, and by the reproducibility of several runs (Pattison and Newton 1989). Nevertheless, establishing that the runs are not strictly reversed or bracketed influences the way in which the experimental data are treated in the thermodynamic modelling described in Part 2. Moreover, the effects of variations in Na, Ca and Al in the final Cpx compositions have to be accounted for in addition to temperature and pressure in the analysis of the final Fe/Mg compositions, and therefore $K_D(Grt-Cpx)$.

Selection of equilibrium compositions and choice of final analyses

The outermost parts of the Cpx grains with the largest newly-formed rims are believed to represent the most equilibrated compositions in each run. In all reanalysed runs, these locations showed the largest differences in composition compared to the starting seed material.

In addition to the reanalysis reported here, the original EDS analyses from PN's study were re-examined because a few of the reported clinopyroxene analyses in their main data table (PN's Table 3) showed suspect stoichiometry. This resulted in omission of about 5% of PN's runs and minor changes to a further 10% of PN's runs. One of the omitted runs was the single result at 700° C, owing to the lack of demonstrable change outside of the heterogeneity range of the starting Cpx. A final set of optimal analyses (Table 1) was obtained by combining the best analyses of the re-examined probe data of PN and the new analyses obtained in this study. Of the 125 analyses listed in Table 1, 82 are from the original PN study and 43 are from the reanalysis in this study; of the 69 reanalysed runs, 43 are from the reanalysis and 26 are from the original PN data. Overall, the magnitude of changes from the PN data were minor, rarely exceeding 2% $Mg \neq .$ The data in Table 1 were optimized prior to any thermodynamic modelling, using experimental and analytical criteria alone, and provide the final input data for the thermodynamic modelling in Part 2.¹

For some pairs of runs with different starting Cpx, an overlap in the final Cpx compositions was observed.

This effect occurred principally in the 1100° C and 1200°C runs, and may be partly an artefact of probing adjacent rims of overlapping garnet and clinopyroxene in the welded run products (see Figs. 1c.1d). Because of progressively lower Ca-contents and higher Al-contents of Cpx in higher temperature runs, stoichiometric criteria to distinguish between Cpx and garnet became more and more equivocal, especially for runs involving high-Ca garnets. However, because Cpx is always more Mg-rich than garnet, possible overlap problems for Cpx approaching more Mg-rich compositions from an Fe-rich starting composition could not lead to overestimation of the Cpx Mg#. Consequently, these runs are the more reliable. Another process that may have led to overlap in Cpx compositions was local change of garnet composition (Mg#) in the vicinity of Cpx crystals, although such changes were rarely found and the magnitude of such changes where found was generally minor.

Comparison between reanalyzed runs and original PN analyses

The results of the reanalysis show no systematic differences from the original PN analyses. For clinopyroxene this is shown in histograms of differences in Na cations, Ca cations, Al cations, X_{jad} , X_{cats} , X_{wo} and Mg #between the reanalysed runs and the original runs. Figures 6A and 6B show histograms for differences in Na cations and Mg#. In all cases the mean and median fall within 0.01 of 0.00 (representing no difference). Thus, although in individual runs there were sometimes differences between this study and PN, there is no consistent difference between the two studies that can be ascribed to differing analytical technique. Significant differences between individual runs are therefore probably due to real compositional differences, such as analysis of relatively more or less equilibrated parts of Cpx grains, and in the 1100° C and 1200° C runs, possible analysis of overlapping Grt and Cpx grains, as discussed above. For the latter runs, the new analyses were favoured in the preparation of the final analysis table, owing to the greater confidence allowed by BSE images.

Assessment of possible problems in PN experiments

Inaccuracy due to EDS analysis

The lack of consistent differences between the reanalysis, which used WDS analysis guided by BSE images,

¹An expanded version of Table 1 including raw oxide analyses is available in spreadsheet format (LOTUS 1-2-3) on request from the Journal.

Table 1 Final clinopyroxene analyses

		Starting Cations for 6 oxygens Fe^{3+}															
Run	P(kbar)	$T(^{\circ}C)$	Grt	Срх		Si	Al	Fe	Mg	Ca	Na	Sum	Mg#	Fe ³⁺	Fe(total	$\overline{)}X$ jad	X cats
74b(1)	15	800	20/14	50	AP	2.001	0.119	0.632	0.403	0.723	0.123	4.001	0.390	0.003	0.004	0.121	0.000
86b(2)	15	800	20/14	20	PN	1.968	0.078	0.667	0.440	0.813	0.055	4.020	0.397	0.041	0.061	0.014	0.032
74a(1)	15	800	20/29	90	AP	1.978	0.103	0.370	0.651	0.833	0.075	4.009	0.638	0.017	0.047	0.058	0.022
74a(2)	15	800	20/29	50	AP	1.969	0.132	0.389	0.646	0.787	0.087	4.009	0.624	0.017	0.044	0.070	0.031
76b(1)	15	800	20/43	90	PN	1.944	0.200	0.277	0.705	0.771	0.118	4.015	0.718	0.030	0.107	0.088	0.056
766(2)	15	800	20/43	50	AP	1.974	0.209	0.235	0.678	0.759	0.132	3.988	0.743	0.000	0.000	0.132	0.051
76a(1)	15	800	20/57	90 50	AP	1.955	0.155	0.182	0.781	0.875	0.043	3.990	0.811	0.000	0.000	0.043	0.066
70a(2)	15	800	20/37	50	AP	1.949	0.108	0.215	0.701	0.834	0.082	4.008	0.780	0.010	0.077	0.065	0.051
67a	15	900	20/14	50	PN	1.950	0.088	0.749	0.462	0.757	0.000	4.006	0.381	0.012	0.016	0.000	0.038
85b	15	900	20/14	20	AP	1.973	0.098	0.712	0.430	0.742	0.044	3.999	0.377	0.000	0.000	0.044	0.028
62a(1)	15	900	20/29	90	PN	1.946	0.111	0.445	0.690	0.808	0.000	3.999	0.608	0.000	0.000	0.000	0.056
62a(2)	15	900	20/29	50	PN	1.962	0.097	0.441	0.690	0.800	0.000	3.990	0.610	0.000	0.000	0.000	0.059
64a(2)	15	900	20/43	50	PN	1.936	0.174	0.336	0.675	0.812	0.091	4.023	0.668	0.046	0.138	0.045	0.064
62b(1)	15	900	20/57	90	PN	1.973	0.113	0.255	0.815	0.785	0.059	4.000	0.762	0.001	0.003	0.059	0.027
62b(2)	15	900	20/57	50	PN	1.960	0.153	0.231	0.764	0.819	0.071	3.999	0.768	0.000	0.000	0.971	0.042
72b(1)	15	1000	20/14	50	\mathbf{AP}	1.961	0.094	0.744	0.389	0.794	0.021	4.002	0.343	0.005	0.007	0.016	0.039
72b(2)	15	1000	20/14	20	PN	1.936	0.110	0.847	0.410	0.706	0.000	4.009	0.326	0.018	0.021	0.000	0.046
80a(1)	15	1000	20/29	90	AP	1.961	0.089	0.507	0.646	0.782	0.019	4.004	0.560	0.008	0.017	0.011	0.039
80a(2)	15	1000	20/29	50	AP	1.960	0.112	0.465	0.638	0.797	0.025	3.997	0.578	0.000	0.000	0.025	.0.046
60a(2)	15	1000	20/57	50	PN	1.946	0.176	0.251	0.756	0.837	0.000	3.966	0.750	0.000	0.000	0.000	0.122
69c	15	1100	20/14	50	\mathbf{PN}	1.915	0.191	0.783	0.436	0.629	0.067	4.023	0.358	0.045	0.058	0.022	0.085
69d	15	1100	20/14	20	\mathbf{PN}	1.862	0.344	0.683	0.355	0.664	0.114	4.023	0.342	0.046	0.067	0.069	0.138
61a	15	1100	20/29	90	AP	1.886	0.360	0.443	0.540	0.635	0.142	4.005	0.549	0.010	0.023	0.131	0.114
61b	15	1100	20/29	50	PN	1.893	0.339	0.432	0.514	0.683	0.154	4.015	0.544	0.029	0.068	0.125	0.107
71d	15	1100	20/43	90	AP	1.898	0.338	0.353	0.534	0.743	0.134	4.000	0.602	0.001	0.002	0.134	0.102
101d	15	1100	20/43	50	PN	1.934	0.261	0.367	0.659	0.666	0.097	3.984	0.642	0.000	0.000	0.097	0.098
66a	15	1100	20/57	90	PN	1.906	0.236	0.329	0.815	0.653	0.074	4.013	0.712	0.027	0.081	0.047	0.094
101b	15	1100	20/57	50	PN	1.897	0.295	0.332	0.773	0.608	0.101	4.006	0.699	0.013	0.039	0.088	0.103
70d	15	1200	20/29	90	AP	1.887	0.283	0.487	0.589	0.690	0.069	4.006	0.547	0.011	0.023	0.058	0.113
88a	15	1200	20/29	50	AP	1.909	0.295	0.455	0.560	0.666	0.115	4.000	0.551	0.001	0.002	0.114	0.091
88b	15	1200	20/43	90	AP	1.886	0.311	0.445	0.630	0.648	0.080	3.999	0.586	0.000	0.000	0.080	0.117
70c	15	1200	20/43	50	AP	1.896	0.313	0.396	0.661	0.638	0.089	3.992	0.626	0.000	0.000	0.089	0.120
70a	15	1200	20/57	90	\mathbf{PN}	1.855	0.362	0.321	0.796	0.585	0.088	4.008	0.713	0.016	0.049	0.073	0.145
70Ь	15	1200	20/57	50	AP	1.906	0.270	0.303	0.928	0.511	0.081	3.999	0.754	0.000	0.000	0.081	0.095
75b(1)	15	800	25/33	90	\mathbf{PN}	1.967	0.062	0.321	0.766	0.887	0.000	4.002	0.705	0.004	0.012	0.000	0.020
75b(2)	15	800	25/33	50	\mathbf{PN}	1.968	0.090	0.317	0.751	0.860	0.000	3.987	0.703	0.000	0.000	0.000	0.058
77a(1)	15	900	25/33	90	\mathbf{PN}	1.941	0.144	0.336	0.698	0.840	0.056	4.015	0.675	0.030	0.090	0.026	0.059
77a(2)	15	900	25/33	50	AP	1.961	0.129	0.335	0.682	0.853	0.027	3.988	0.670	0.000	0.000	0.027	0.064
80b(1)	15	1000	25/33	90	AP	1.936	0.146	0.369	0.654	0.880	0.013	3.998	0.639	0.000	0.000	0.013	0.069
80b(2)	15	1000	25/33	50	AP	1.939	0.135	0.387	0.665	0.859	0.015	4.001	0.632	0.002	0.004	0.014	0.061
71a	15	1100	25/33	90	AP	1.817	0.440	0.454	0.582	0.625	0.090	4.008	0.562	0.016	0.036	0.074	0.183
71b	15	1100	25/33	50	PN	1.843	0.431	0.357	0.592	0.648	0.139	4.011	0.624	0.022	0.061	0.117	0.157
88c	15	1200	25/33	90	AP	1.892	0.291	0.467	0.511	0.763	0.076	4.000	0.523	0.001	0.001	0.076	0.108
88d	15	1200	25/33	50	PN	1.837	0.389	0.422	0.547	0.741	0.064	4.000	0.565	0.001	0.001	0.063	0.163
23a	15	800	30/14	50	AP	1.959	0.125	0.568	0.492	0.829	0.012	3.985	0.464	0.000	0.000	0.012	0.071
23b	15	800	30/14	20	\mathbf{PN}	1.985	0.070	0.594	0.470	0.861	0.000	3.980	0.442	0.000	0.000	0.000	0.055
98a(1)	15	800	30/21	90	PN	1.949	0.096	0.370	0.682	0.888	0.033	4.019	0.648	0.037	0.101	0.000	0.046
98a(2)	15	800	30/21	50	PN	1.967	0.096	0.366	0.628	0.902	0.052	4.011	0.632	0.022	0.060	0.030	0.033
98b(1)	15	800	30/29	90	PN	1.969	0.128	0.295	0.656	0.882	0.074	4.004	0.690	0.008	0.028	0.066	0.031
98b(2)	15	800	30/29	50	PN	1.961	0.130	0.313	0.667	0.870	0.063	4.005	0.681	0.010	0.031	0.053	0.039
34a	15	800	30/43	90	PN	1.966	0.130	0.214	0.739	0.920	0.000	3.969	0.775	0.000	0.000	0.000	0.096
53a	15	800	30/43	50	PN	1.967	0.112	0.249	0.746	0.904	0.000	3.977	0.750	0.000	0.000	0.000	0.078
4a	15	800	30/57	90	PN	1.990	0.050	0.174	0.837	0.935	0.000	3.985	0.828	0.000	0.000	0.000	0.039
330	15	800	30/37	50	PIN	2.014	0.123	0.209	0.721	0.824	0.063	5.936	0.775	0.000	0.000	0.063	0.074
21a	15	900	30/14	50	PN	1.967	0.059	0.614	0.461	0.904	0.000	4.004	0.429	0.008	0.013	0.000	0.026
21b	15	900	30/14	20	PN	1.969	0.080	0.638	0.449	0.855	0.000	3.991	0.413	0.000	0.000	0.000	0.049
77b(1)	15	900	30/21	90 50	AP	1.969	0.122	0.425	0.575	0.856	0.045	3.992	0.575	0.000	0.000	0.045	0.047
77b(2)	15	900	30/21	50	PN	1.956	0.121	0.431	0.615	0.861	0.000	3.984	0.588	0.000	0.000	0.000	0.077
20a 201-	15	900	30/29	90 50	PN DN	1.939	0.114	0.325	0.703	0.853	0.060	4.014	0.084	0.029	0.088	0.031	0.041
200 225	15	900 000	30/29 20/42	50 50	PN DN	1.903	0.099	0.394	0.023	0.872	0.072	4.024	0.014	0.047	0.121	0.024	0.037
329	15	200 900	30/43	90	ΓΊΝ ΔΡ	1.900	0.106	0.270	0.743	0.020	0.000	3 007	0.750	0.000	0.000	0.000	0.008
32h	15	900	30/57	50	PN	1.909	0.299	0.172	0.688	0.807	0.128	4.005	0.800	0.010	0.059	0.118	0.091

Table 1 (continued)

			Starti	ng		Cati	ons for	6 oxyg	ens						Fe ³⁺		
Run	P(kbar)	$T(^{\circ}C)$) Grt	Срх		Si	Al	Fc	Mg	Ca	Na	Sum	Mg#	Fe ³⁺	Fe(total	$\bar{)}X$ jad	Xcats
28a	15	1000	30/14	50	AP	1.970	0.173	0.598	0.392	0.762	0.096	3.991	0.396	0.000	0.000	0.096	0.048
28b	15	1000	30/14	20	PN	1.924	0.224	0.639	0.353	0.788	0.071	3.999	0.356	0.000	0.000	0.071	0.077
99b(1)	15	1000	30/29	90	PN	1.899	0.190	0.403	0.616	0.884	0.028	4.020	0.605	0.040	0.099	0.000	0.089
99b(2)	15	1000	30/29	50	PN	1.919	0.156	0.404	0.633	0.880	0.020	4.013	0.611	0.025	0.063	0.000	0.075
29a 20b	15	1000	30/43	90 50	PN DN	1.898	0.253	0.250	0.681	0.869	0.051	4.001	0.732	0.002	0.009	0.049	0.102
290 27a	15	1000	30/43	90	ΔΡ	1.927	0.200	0.520	0.044	0.829	0.069	3 000	0.008	0.029	0.090	0.060	0.075
27b	15	1000	30/57	50	PN	1.878	0.329	0.207	0.677	0.834	0.068	3.992	0.766	0.000	0.000	0.050	0.035
68c	15	1100	30/14	50	PN	1.863	0.355	0.617	0.329	0.737	0.116	4.017	0.348	0.035	0.056	0.081	0.137
50b	15	1100	30/14	20	PN	1.952	0.290	0.563	0.312	0.699	0.174	3.989	0.357	0.000	0.000	0.174	0.069
57a	15	1100	30/21	50	AP	1.934	0.274	0.491	0.405	0.765	0.122	3.990	0.452	0.000	0.000	0.122	0.086
57b	15	1100	30/21	20	PN	1.829	0.444	0.462	0.424	0.726	0.131	4.015	0.479	0.029	0.063	0.101	0.171
69a 69b	15	1100	30/29	90 50		1.876	0.363	0.381	0.518	0.752	0.103	3.994	0.576	0.000	0.000	0.103	0.136
102a	15	1100	30/43	90	PN	1.908	0.331	0.393	0.430	0.728	0.101	2.997	0.557	0.000	0.000	0.101	0.098
102b	15	1100	30/43	50	AP	1.868	0.415	0.218	0.600	0.753	0.141	3.996	0.733	0.000	0.000	0.000	0.088
102c	15	1100	30/57	90	PN	1.846	0.392	0.203	0.675	0.809	0.066	3.991	0.769	0.000	0.000	0.066	0.172
102d	15	1100	30/57	50	PN	1.818	0.485	0.180	0.614	0.781	0.123	4.001	0.773	0.002	0.011	0.121	0.182
56a	15	1200	30/29	90	PN	1.789	0.479	0.472	0.502	0.696	0.067	4.004	0.516	0.009	0.019	0.058	0.211
79c	15	1200	30/29	50	AP	1.785	0.561	0.352	0.426	0.742	0.134	4.001	0.548	0.002	0.005	0.132	0.215
47a 47b	15	1200	30/43	90 50	AP	1.806	0.420	0.411	0.580	0.752	0.030	3.999	0.585	0.000	0.000	0.030	0.196
470 45a	15	1200	30/43	90	ΔP	1.801	0.341	0.338	0.041	0.762	0.050	3.993	0.655	0.000	0.000	0.050	0.155
45b	15	1200	30/57	50	PN	1.825	0.425	0.240	0.645	0.828	0.000	3.962	0.729	0.000	0.000	0.027	0.137
93a(1)	15	800	40/21	90	PN	1.951	0.181	0.311	0.645	0.828	0.085	4.001	0.675	0.002	0.008	0.083	0.230
93a(2)	15	800	40/21	50	PN	1.925	0.228	0.325	0.575	0.867	0.080	4.000	0.639	0.001	0.002	0.079	0.075
93b(1)	15	800	40/57	90	PN	1.864	0.400	0.130	0.680	0.817	0.089	3.980	0.839	0.000	0.000	0.089	0.175
93b(2)	15	800	40/57	50	PN	1.902	0.256	0.138	0.745	0.892	0.074	4.008	0.844	0.015	0.109	0.059	0.098
90a(2)	15	900	40/21	50	PN	1.895	0.275	0.356	0.542	0.849	0.103	4.019	0.604	0.039	0.109	0.064	0.105
90b(2)	15	900	40/57	50	PN	1.838	0.373	0.169	0.689	0.871	0.073	4.012	0.803	0.024	0.143	0.048	0.162
89a 201	15	1000	40/21	90 50	PN DN	1.895	0.238	0.409	0.546	0.898	0.000	3.986	0.572	0.000	0.000	0.000	0.133
91a(1)	15	1000	40/21 40/57	90	EN PN	1.900	0.228	0.425	0.500	0.801	0.000	3.980	0.308	0.000	0.000	0.000	0.134
91a(2)	15	1000	40/57	50	PN	1.812	0.400	0.182	0.656	0.899	0.000	3.975	0.782	0.000	0.000	0.000	0.205
92a	15	1100	40/21	90	AP	1.830	0.443	0.415	0.415	0.790	0.109	4.003	0.500	0.006	0.014	0.103	0.170
92b	15	1100	40/21	50	AP	1.859	0.437	0.375	0.403	0.782	0.133	3.989	0.518	0.000	0.000	0.133	0.163
92c	15	1100	40/57	90	AP	1.738	0.619	0.164	0.534	0.854	0.087	3.996	0.765	0.000	0.000	0.087	0.270
92d	15	1100	40/57	50	AP	1.776	0.583	0.176	0.533	0.809	0.111	3.988	0.752	0.000	0.000	0.111	0.248
94c	15	1200	40/57	90 50	PN	1.662	0.749	0.192	0.523	0.803	0.072	4.000	0.732	0.000	0.000	0.072	0.339
940	15	1200	40/57	50	PN	1.733	0.607	0.227	0.563	0.796	0.077	4.002	0.713	0.005	0.021	0.072	0.267
90a(1) 96a(2)	15	800	50/21 50/21	90 50	PN DM	1.957	0.178	0.297	0.630	0.852	0.082	3.995	0.679	0.000	0.000	0.082	0.053
96h(1)	15	800	50/57	90	PN	1.943	0.179	0.330	0.000	0.872	0.071	4.003	0.041	0.007	0.020	0.065	0.057
96b(2)	15	800	50/57	50	PN	1.858	0.381	0.122	0.644	0.899	0.095	3.999	0.841	0.000	0.000	0.095	0.144
95a(1)	15	900	50/21	90	PN	1.911	0.247	0.322	0.577	0.859	0.096	4.013	0.642	0.026	0.082	0.070	0.089
95b(1)	15	900	50/57	90	PN	1.914	0.224	0.130	0.773	0.932	0.000	3.974	0.856	0.000	0.000	0.000	0.138
95b(2)	15	900	50/57	50	PN	1.834	0.458	0.130	0.612	0.845	0.116	3.995	0.825	0.000	0.000	0.116	0.175
97a(1)	15	1000	50/21	90	PN	1.861	0.265	0.345	0.577	0.943	0.031	4.022	0.626	0.044	0.126	0.000	0.126
9/a(2)	15	1000	50/21	50	PN	1.853	0.288	0.369	0.545	0.934	0.031	4.019	0.596	0.038	0.102	0.000	0.140
97b(1) 97b(2)	15	1000	50/57	90 50	PN	1.738	0.493	0.137	0.660	0.931	0.035	4.013	0.828	0.027	0.196	0.008	0.242
100a	15	1100	50/21	90	AP	1.720	0.540	0.141	0.382	0.951	0.028	3 005	0.820	0.050	0.210	0.000	0.272
100b	15	1100	50/21	50	AP	1.795	0.504	0.391	0.352	0.865	0.095	4.001	0.324	0.000	0.000	0.101	0.219
100c	15	1100	50/57	90	AP	1.841	0.432	0.188	0.581	0.858	0.086	3.986	0.755	0.000	0.000	0.086	0.187
100d	15	1100	50/57	50	PN	1.828	0.427	0.228	0.573	0.860	0.085	4.001	0.716	0.002	0.010	0.083	0.172
82a(1)	29	1000	30/14	50	PN	1.954	0.079	0.628	0.481	0.834	0.061	4.037	0.433	0.074	0.117	0.000	0.033
87b(1)	29	1000	30/21	90 50	PN	1.956	0.129	0.443	0.607	0.845	0.000	3.979	0.578	0.000	0.000	0.000	0.085
δ/D(2) 87a(1)	29 29	1000	30/21 30/20	50 90	AP AD	1.984	0.077	0.413	0.604	0.884	0.029	3.991	0.594	0.000	0.000	0.029	0.033
87a(1)	29 29	1000	30/29	50 50	AP	1.900	0.101	0.392	0.653	0.898	0.019	3.999 3.999	0.017	0.000	0.000	0.019	0.042
82b(1)	29	1000	30/57	90 90	PN	1.972	0.129	0.207	0.779	0.876	0.000	3.963	0.790	0.000	0.000	0.010	0.101
82b(2)	29	1000	30/57	50	PN	1.964	0.127	0.227	0.785	0.868	0.000	3.972	0.775	0.000	0.000	0.000	0.002
Total nu	mber of	runs:	125			~			Avera	ge:		3.999		0.009	0.027		

^a Note: Starting Grt = $\chi_{ca}/Mg\#$; starting Cpx = Mg# *PN*: Pattison and Newton (1989); *AP*: this study



Fig. 6A,B Histograms of differences in Cpx compositions between the reanalysed runs of this study (AP, WDS) and the original results of PN (PN, EDS). A $100 \times Na$ cations for 6 oxygens. B 100 Mg #

and the original PN study, which used EDS analysis, suggests that no significant inaccuracies were introduced by the analytical techniques employed in this study or the original PN study.

Na

The reanalysis confirms the small but variable amounts of Na reported in PN (Table 1). Most but not all product Cpx compositions contain some Na, in contrast to the inserted starting Cpx (and Grt) compositions which are Na-free. Although Na is generally higher in the higher temperature runs, there are numerous exceptions which suggest that the abundance of Na in the final clinopyroxenes is controlled by how much Na was introduced into the experimental charges. The most likely sources for the Na arc either from small amounts of pressure medium glass that invaded the graphite containers used in garnet synthesis, and which may have been subsequently mixed in with the garnet starting material, or possibly diffusion of Na into the experimental charges from the pressure medium during the runs. As found by PN there is no discernible relationship between Na content and Mg#, although this observation should not be extrapolated from the relatively Na-poor clinopyroxenes in PN's study (Na cations mostly less than 0.12) to more Na-rich clinopyroxenes.

Fe³⁺

The average Fe^{3+}/Fe_{total} for all runs in the final table of analyses is 0.027, as calculated from stoichiometry using the scheme of Lindsley (1983). Owing to the uncertainities in such a calculation scheme, the value obtained is not significantly different from 0.00, although equally it is probably not significantly different from 0.10. Calculated Fe^{3+} contents showed no correlation with respect to P, T or other compositional parameters. Consequently, there is no evidence for anomalous Fe³⁺ contents which might have had a significant effect on the final Cpx Mg#, and hence $K_{\rm D}$ (Grt-Cpx). The calculated Fe³⁺ values are comparable to those calculated using the same scheme for clinopyroxenes in natural granulites (e.g. Pattison 1991). A possible correlation between high Na content and high Fe³⁺ content (indicating a significant acmite component in the product clinopyroxene) was searched for, but none was found; although some Na-rich analyses were Fe³⁺-rich, several relatively Na-rich analyses contain negligible calculated Fe³⁺, and vice versa.

Variable Ca and Al content of Cpx

As reported by PN, Ca and Al in Cpx show significant variations as a function of temperature, pressure and composition, even though they are unreversed and unbracketed, and on an individual basis show scatter (Figs. A–C). X_{cats} shows increases with each of temperature, Mg# of Cpx and Ca-content of garnet. The dependency of X_{cats} on Mg# of Cpx varies markedly as a function of Ca-content of coexisting garnet: the dependency is subtle for $X_{Ca}^{Grt} = 0.2$, significant for $X_{Ca}^{Grt} = 0.3$, and extreme for $X_{Ca}^{Grt} = 0.4$ and 0.5 (Figs. 7A–C).

Thermocouple poisoning

No direct methods were applied to test for the thermocouple poisoning. Indirect evidence bearing on





Fig 7A–C Plots of X_{cats} in Cpx versus Mg # in Cpx for different temperatures and grossular contents of garnet. A $X_{Ca}^{Grt} = 0.2$, B $X_{Ca}^{Grt} = 0.3$, C $X_{Ca}^{Grt} = 0.4$. The *dotted lines* are estimated by eye

possible thermocouple poisoning is provided by monitoring of power output during the experiments: if power output required to maintain the same apparent (i.e. thermocouple) temperature increases or decreases with time during the experiment, thermocouple poisoning may be indicated, whereas if power output remains uniform or shows minor (< 5%) random oscillations throughout the experiment, there is no evidence for significant thermocouple poisoning. In PN's experiments, power output was monitored in most cases daily (sometimes, more, depending on the duration of the runs), and rarely showed more than 5% random variation. Consequently, thermocouple poisoning is not thought to be a significant source of inaccuracy in PN's experiments.

Uncertainty in garnet and clinopyroxene analyses

Even though garnet compositions after the runs still showed considerable heterogeneity (Table 2, Figs. 8A, 8B), the mean composition was generally within 0.02 of the nominal starting garnet composition. The absolute range generally coincided with or exceeded the range reported in Table 1 of PN, probably due to the larger number of analyses obtained in the reanalysis and possible compositional changes during the runs. The degree of garnet heterogeneity is most likely a function of the grain size of the mixed end member glasses from which the garnet was crystallized (see description of synthesis technique in PN).

Because no textural or compositional criteria allowed unequivocal selection of the equilibrium garnet compositions in the runs, all that can be concluded is that the equilibrium composition must lie somewhere within the measured range. However, given the generally normal distribution around the mean (Fig. 8), which is generally within Mg# = 0.01 of the nominal composition, a reasonable uncertainty range is ± 0.03 of the nominal composition, which corresponds approximately to a 1-sigma uncertainty envelope. This uncertainity range additionally accommodates the small core-rim variations in garnet after some of the runs noted above. For final clinopyroxene rim compositions, uncertainty arising from analytical technique is conservatively estimated as ± 0.015 in Mg#.

Assessment of the technique of garnet buffering

Garnet showed little to no evidence for significant change during the experimental runs, apart from minor changes in Mg # (< 0.02) consistent with mass balance considerations. The fact that these compositional changes were smaller than uncertainities in the starting compositions supports the validity of the technique of



Fig. 8A,B Histograms of garnet compositions after runs. A Run 23b: 15 kbar, 800° C, 352 h; starting Cpx-Di₂₀; starting Grt- $X_{Ca} = 0.3$, Mg # = 0.14. **B** Run 27b: 15 kbar, 1000° C, 22 h; starting Cpx-Di₅₀; starting Grt- $X_{Ca} = 0.3$, Mg # = 0.57

garnet buffering by overwhelming abundance. However, because the equilibration mechanism involved multi-component solution-precipitation, the experiments do not provide strictly reversed or bracketing data.

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Table	2 Garnet	compositions
from 1	reanalyzed	runs

Nominal start Grt 100X _{Ca}	100Mg#	No. runs	No. points	Mean 100Mg#	Range 100Mg #	Mean 100X _{Ca}	Range 100X _{Ca}
20	14	9	178	14	10-18	20	18 23
20	29	8	164	28	23-33	21	17-23
20	43	5	87	42	39-46	20	18 - 22
20	57	5	113	55	50-60	19	18 - 23
25	33	7	83	32	25-37	26	18-37
30	14	6	107	14	10-18	28	26-31
30	21	2	29	19	17-22	30	27-32
30	29	6	74	30	25-34	31	24-33
30	43	8	163	42	35-47	29	24-34
30	57	8	157	56	49-62	30	25-33
40	21	2	26	22	19-26	41	37-42
40	57	2	18	55	49-58	39	34-41
50	21	2	24	20	18-23	51	47-54
50	57	2	24	55	50-63	51	43-65

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