

## Order-disorder experiments on orthopyroxenes: Implications for the orthopyroxene geospeedometer\*

LAWRENCE M. ANOVITZ,\*\* ERIC J. ESSENE

Department of Geological Sciences, The University of Michigan, Ann Arbor, Michigan 48109, U.S.A.

WILLIAM R. DUNHAM

Department of Biophysics, The University of Michigan, Ann Arbor, Michigan 48109, U.S.A.

### ABSTRACT

Reversed experiments have been performed to better constrain the equilibrium partitioning of Fe between the M1 and M2 sites in orthopyroxene and the kinetics of the ordering process. Two samples (M32b,  $X_{\text{Fe}} = 0.388$ ; PX4-TM2,  $X_{\text{Fe}} = 0.813$ ) were experimentally disordered at 900 °C and ordered at 500, 600, 700, and 800 °C for various times between  $3 \times 10^2$  and  $4 \times 10^6$  s. Reversals were obtained by heating naturally ordered materials that had not been disordered in advance in order to better constrain the equilibrium ordering state. Ordering and redox states of the pyroxenes were determined using Mössbauer spectroscopy. Results suggest that the equilibrium ordering state for a given composition and temperature is more disordered than predicted by the model of Ganguly (1982). Fitting the data to the equation of Saxena and Ghose (1971) yields  $\ln K = 1203.30/T + 0.1272$  ( $T$  in kelvins),  $\bar{W}^{\text{M1}} = 5449$  J/mol, and  $\bar{W}^{\text{M2}} = 2083$  J/mol.

A strong dependence of the kinetic data on composition is suggested by the combination of all available rate data. Calculations performed using these data yield cooling rates for many metamorphic terranes of 0.1 to 100 °C/m.y., which are significantly slower than those previously obtained from pyroxene-ordering studies. These rates are within the range suggested by other approaches. The relatively large error ranges obtained, however, suggest that additional calibration is necessary at lower temperatures and with Fe-, Ca-, and Al-rich compositions. Studies of ordering in orthopyroxenes may be a useful method for obtaining cooling rates in igneous and contact-metamorphic environments.

### INTRODUCTION

In recent years petrologists have attempted to couple time as a variable with calculations of metamorphic pressures and temperatures (Lasaga et al., 1977; Berger and York, 1981; Ganguly, 1982; Lasaga, 1983). One approach to calculation of time versus temperature paths is an examination of the kinetics of ordering of Fe between the M1 and M2 sites in orthopyroxenes (Ganguly, 1982). This calculation requires that accurate data be available for both the equilibrium distribution and kinetics of re-equilibration as a function of temperature and composition. Several studies have previously been undertaken to obtain these data for orthopyroxenes (Virgo and Hafner, 1969, 1970; Saxena and Ghose, 1971; Khristoforov et al., 1974; Besancon, 1981a; Grammenopoulou, 1981; Domeneghetti et al., 1985; Sykes and Molin, 1986). Unfortunately, calculations for orthopyroxenes from regional metamorphic terranes based on these data (Besancon, 1981b; Ganguly, 1982; Saxena and Dal Negro, 1983) have

yielded unreasonably fast cooling rates ( $10^{-1}$  to  $10^{+2}$  °C/yr). Geophysical modeling of the cooling rates of metamorphic terranes (England and Thompson, 1984; Hodges and Royden, 1984; Royden and Hodges, 1984; Thompson and England, 1984; Malhe et al., 1986) suggest cooling rates of 0.1 to 10 °C/m.y. Calculations based on  $^{39}\text{Ar}/^{40}\text{Ar}$  measurements (Berger and York, 1981) and garnet-diffusion studies (Lasaga, 1983) yield similar results. We have therefore undertaken a series of kinetic and reversed equilibrium experiments in order to test whether the apparent errors in the orthopyroxene speedometer are due to poor calibration of the data base.

### ORDER-DISORDER MODELS

The theoretical basis for the orthopyroxene geospeedometer has been described in detail by Ganguly (1982) and will only be summarized here. The equilibrium ordering of Fe and Mg in orthopyroxene may be described as



for which the intrasite cation-distribution constant ( $K_D$ ) is written

$$K_D = X_{\text{Mg}}^{\text{M1}} X_{\text{Fe}}^{\text{M2}} / X_{\text{Mg}}^{\text{M2}} X_{\text{Fe}}^{\text{M1}}. \quad (2)$$

\* Contribution no. 446 from the Mineralogical Laboratory, The University of Michigan.

\*\* Present address: Department of Geosciences, University of Arizona, Tucson, Arizona 85721, U.S.A.

Saxena and Ghose (1971) suggested that the equation

$$RT \ln K_D = RT \ln K + \bar{W}^{M1}(1 - 2X_{Fe}^{M1}) - \bar{W}^{M2}(1 - 2X_{Fe}^{M2}) \quad (3)$$

could be used to describe  $K_D$  as a function of temperature and composition. An expanded equation has been suggested (Thompson, 1969, 1970; Grover, 1980; Sack, 1980; Davidson, 1985):

$$RT \ln K_D = RT \ln K + \Delta G_c(X_{Fe}^{M1} - X_{Fe}^{M2}) + \bar{W}^{M1}(1 - 2X_{Fe}^{M1}) - \bar{W}^{M2}(1 - 2X_{Fe}^{M2}) \quad (4)$$

The new variable  $\Delta G_c$  represents the free-energy difference for the composition  $Fe_{0.5}Mg_{0.5}SiO_3$  between that obtained by mechanical mixing and the average energy of the ordered and anti-ordered states (Davidson, pers. comm.). Sack (1980) and Ganguly (1986) noted that the  $\bar{W}$  terms in Equation 3 implicitly contain a Bragg-Williams term. Thus  $\Delta G_c$  is not set to zero in Equation 3, but is included implicitly in the  $\bar{W}$  terms, and the  $\bar{W}$  terms in Equations 3 and 4 are not strictly equivalent. Unfortunately the available equilibrium data are not sufficiently well constrained to warrant the use of the more complex equation, and in this paper the simpler equation (Eq. 3) has been adopted.

Mueller (1969) described the kinetics of intracrystalline ordering by treating the process as one controlled by a single mechanism. Khristoforov et al. (1974) have argued that their data are better described by a two-stage model; however, Besancon (1981a) showed that Mueller's model is adequate to fit both the data of Khristoforov et al. and Besancon (1981a). Mueller's model is adopted here. The rate constant  $C_0\bar{K}$  is described by the equation

$$-C_0\bar{K}\Delta t = (b^2 - 4ac)^{-0.5} \left[ \ln \frac{|(2a\bar{X}_i^\alpha + b) - (b^2 - 4ac)^{0.5}|}{(2a\bar{X}_i^\alpha + b) + (b^2 - 4ac)^{0.5}} \right]_{X_i^\alpha(t_0)}^{\bar{X}_i^\alpha(t)} \quad (5)$$

when, for ordering,

$$(2a\bar{X}_i^\alpha + b) > |(b^2 - 4ac)^{0.5}| \quad (6)$$

and

$$-C_0\bar{K}\Delta t = (b^2 - 4ac)^{-0.5} \left[ \ln \frac{|(b^2 - 4ac)^{0.5} - (2a\bar{X}_i^\alpha + b)|}{(2a\bar{X}_i^\alpha + b) + (b^2 - 4ac)^{0.5}} \right]_{X_i^\alpha(t_0)}^{\bar{X}_i^\alpha(t)} \quad (7)$$

when, for disordering,

$$(2a\bar{X}_i^\alpha + b) < |(b^2 - 4ac)^{0.5}|. \quad (8)$$

The above equations have been simplified as

$$a = p(1 - (1/K_D)) \quad (9)$$

$$b = q - X_i + (X_i + p)/K_D \quad (10)$$

$$c = -X_i/K_D, \quad (11)$$

where  $X_i$  is the mole fraction of Fe in the bulk analysis,  $\bar{X}_i^\alpha$  is the mole fraction of Fe in the site of interest, and  $p$  and  $q$  are the fractions of the total number of sites involved in the order-disorder that are of each type (M1 and M2). For orthopyroxenes, both  $p$  and  $q$  equal 0.5.

Equations 5 and 7 may be simply recast as (Ganguly, 1982)

$$\bar{X}_i^\alpha(t) = \frac{(b^2 - 4ac)^{0.5}(1 + FD) - b(1 - FD)}{2a(1 - FD)} \quad (12)$$

$$F = \exp[-C_0\bar{K}\Delta t(b^2 - 4ac)^{0.5}] \quad (13)$$

$$D = \frac{[2a\bar{X}_i^\alpha(t_0) + b] - (b^2 - 4ac)^{0.5}}{[2a\bar{X}_i^\alpha(t_0) + b] + (b^2 - 4ac)^{0.5}} \quad (14)$$

In order to use these equations to calculate cooling rates, a choice is first made as to the form of the time versus temperature equation (Ganguly, 1982). Ganguly has suggested either an exponential

$$T = T_0 \exp(-\eta t) \quad (15)$$

or asymptotic

$$1/T = 1/T_0 + \eta t \quad (16)$$

model. A first guess is made for the cooling constant  $\eta$ , and a final closure temperature  $T_c$  is calculated. The cooling constant is then varied until the ordering state at the calculated closure temperature is equal to that observed for the natural sample. The calculated closure temperature will in general be greater than the calculated quenching temperature  $T_q$ , which is the temperature below which there is no further change in the ordering state. This difference reflects progressive disequilibrium in the ordering state of the sample as temperature approaches  $T_q$ .

## PREVIOUS EXPERIMENTAL WORK

Previous authors have studied the time versus temperature dependence of ordering in orthopyroxenes (Virgo and Hafner, 1969; Saxena and Ghose, 1971; Khristoforov et al., 1974; Besancon, 1981a; Grammenopoulou, 1981; Domeneghetti et al., 1985; Sykes and Molin, 1986; Besancon et al., unpub.). Of these studies, Saxena and Ghose (1971), Grammenopoulou (1981), Sykes and Molin (1986), and Besancon, Sposato, and Grover (written comm.) only examined equilibrium ordering, whereas the others acquired data applicable to both equilibrium and kinetic studies.

Figure 1 summarizes the results of the equilibrium experiments at 500, 600, 700, 750, 800, and 850 °C. Virgo and Hafner's (1969) data at 1000 °C have been excluded, as their samples probably reset during cooling (Ganguly, 1982). The arrows in each figure begin at the initial ordering state and end at the final state. The model fitted by Ganguly (1982) is shown as the dashed line. An important difference between our interpretation of these data and Ganguly's is that we have treated these experiments as half reversals that limit, but do not necessarily define, the equilibrium. This difference becomes important at 500 °C, where kinetic modeling suggests that runs of 4 months are necessary to reach equilibrium. There is inadequate information to constrain the actual values of the equilibrium ordering state at lower temperatures. At 600 to 850 °C, where the kinetic data suggest that attain-

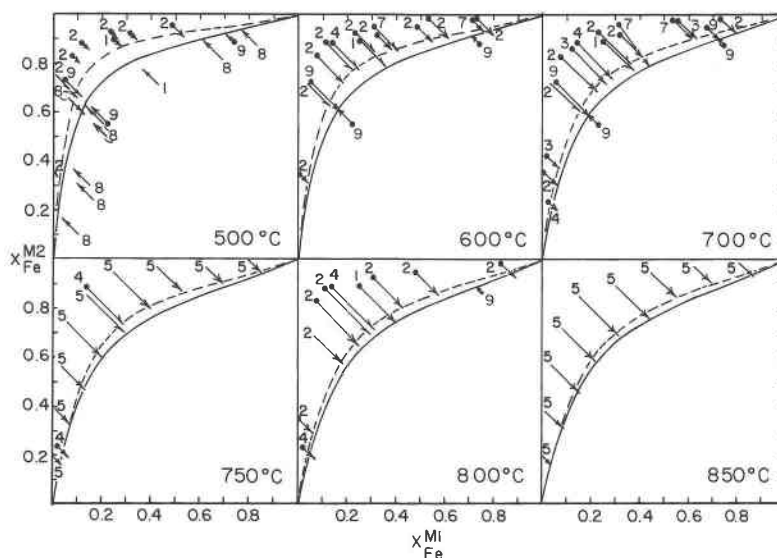


Fig. 1. Equilibrium experiments on the ordering state of Fe in orthopyroxenes as a function of temperature: (1) Virgo and Hafner (1969), (2) Saxena and Ghose (1971), (3) Domeneghetti et al. (1985), (4) Besancon (1981a), (5) Grammenopoulou (1981), (6) Khristoforov et al. (1974), (7) Sykes and Molin (1986), (8) Besancon, Sposato, and Grover (written comm.), (9) this study. Dots indicate initial ordering state; tips of arrowheads show the final state. If dots are not shown, initial values were not given, and reversal directions are inferred. Dashed lines are the model of Ganguly (1982); solid lines are our calculations.

ment of equilibrium is probable, the lack of reversals in the previous experiments makes estimation of the errors involved difficult. Examination of quoted errors ( $X_{Fe}^{M1} = \pm 0.005$  for M32b of this work;  $\pm 0.0022$  for sample 3209 of Virgo and Hafner, 1969;  $\pm 0.01$  for the data of Saxena and Ghose, 1971;  $\pm 0.03$  for sample TZ and  $\pm 0.0018$  for sample HC of Besancon, 1981a;  $\pm 0.01$  for the data of Domeneghetti et al., 1985, and presumably the data of Sykes and Molin, 1986) suggests that these are large enough to account for much of the discrepancy, especially at 700 °C and above.

The data of Khristoforov et al. (1974) suggest much smaller  $K_D$  values than other equilibrium experiments. The length of their experimental runs at 500 °C (up to 240 h) is insufficient for this discrepancy to be due to greater equilibration in their experiments. As this is the only study where NMR was used to measure the ordering state, this technique may be too imprecise for the necessary measurements. Kinetic measurements were also performed by Khristoforov et al. (1974), but because of the difficulties with their equilibrium results, both the equilibrium and kinetic data of Khristoforov et al. have also been ignored.

## EXPERIMENTAL METHODS AND MATERIALS

### Sample description

Two samples were selected for our experiments, M32b and PX4-TM2. Analyses of these materials and other samples from the Grenville province, Ontario, used in this study are given in Table 1. All analyses in this table are normalized to two cations and charge-balanced against three oxygens to estimate the  $Fe^{3+}/Fe^{2+}$  ratio. Mössbauer analyses were not used to obtain the  $Fe^{3+}/Fe^{2+}$  ratio as the amount of  $Fe^{3+}$  was in most cases at or near the

limit of sensitivity of the data-reduction procedures. Sample PX4-TM2 was obtained from the collections of the University of Michigan. Its provenance is not known, but inclusions of garnet and quartz suggest that it came from a granulite-facies terrane. It was a large single crystal (approx.  $10 \times 5 \times 5$  cm) with  $X_{Fe} = 0.813$ . Quartz and garnet inclusions were removed by magnetic separation and hand picking, and hematite staining on cleavage surfaces was removed by washing the sample in oxalic acid.

Sample M32b ( $X_{Fe} = 0.388$ ) was obtained from a rock kindly provided by D. P. Moecher, collected southeast of Parry Sound 4.5 km east of Route 69 on Route 518 in the Grenville province, Ontario. The sample was a single crystal approximately 2 cm on a side in a matrix of garnet, plagioclase, orthopyroxene, hornblende, and ilmenite. The crystal was cut out of the matrix and crushed; quartz and garnet inclusions were removed by magnetic separation and hand picking. No oxalic acid treatment was necessary for this sample. Both crystals were crushed and sieved to between 35 and 100 mesh, and the final sample was hand picked to be sure that only gemmy, inclusion-free material was used for the experiments. Powder X-ray diffraction studies of the samples revealed only peaks identifiable as orthopyroxene.

### Experimental methods

Two sets of experiments (<2 h and >2 h) were conducted on each sample. Runs of 2 h or less were done in a Deltech furnace adapted for gas-mixing. Oxygen fugacity was controlled by two glass manometers using a CO-CO<sub>2</sub> gas mixture and monitored using a zirconia electrolyte. The  $F_{O_2}$  was maintained approximately 0.5 log units above the iron-wüstite buffer (or iron-magnetite buffer at lower temperatures) in order to prevent oxidation of the samples during the experiment. Samples (40 mg) were placed in a Vycor crucible, suspended from a Pt wire, and lowered into a hot furnace with gases flowing. At the completion of the run, an electric current was used to break the suspension wire, and the sample fell 47 cm into liquid N<sub>2</sub>, quenching in less than 1 s.

TABLE 1. Electron-microprobe analyses of pyroxenes used in this study

	A5B	ALG 83C 10	BA7D	BA9A	GRU 83C 15	GRU 84B 1	HAL 84B 40	HUT 83C 9	M20B	M32b	PSO 83C 8	PX4- TM2	REN 84B 7	RIV 83C 22	SAG 80 3
SiO <sub>2</sub>	51.35	51.44	50.36	51.52	52.66	52.55	52.08	51.30	51.95	50.96	51.55	47.15	52.55	52.51	52.43
TiO <sub>2</sub>	0.07	0.14	0.07	0.07	0.07	0.07	0.07	0.00	0.07	0.07	0.00	0.00	0.00	0.14	0.07
Al <sub>2</sub> O <sub>3</sub>	1.55	1.19	1.13	1.03	1.27	0.68	1.21	1.18	1.16	2.33	1.98	0.64	1.04	1.05	1.64
Fe <sub>2</sub> O <sub>3</sub>	0.00	0.00	0.00	1.12	0.07	0.78	0.00	0.07	0.21	1.26	0.99	0.00	0.07	1.07	0.71
Cr <sub>2</sub> O <sub>3</sub>	0.00	0.00	0.00	0.00	0.07	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.07	0.00
FeO	29.02	28.20	31.76	28.29	24.70	26.92	23.44	23.85	26.21	23.39	21.05	45.84	22.13	19.50	24.30
MnO	0.49	0.80	0.90	0.99	0.75	0.38	0.63	0.76	0.93	0.75	0.69	0.33	0.81	0.44	0.32
MgO	17.29	17.67	15.21	17.77	20.43	19.63	20.36	21.03	18.98	20.14	21.88	5.16	21.56	23.31	20.97
CaO	0.58	0.53	0.43	0.54	0.40	0.35	1.29	0.50	0.79	0.64	0.50	0.18	1.04	1.00	0.40
Na <sub>2</sub> O	0.03	0.00	0.00	0.00	0.00	0.03	0.06	0.00	0.03	0.03	0.06	0.02	0.03	0.03	0.06
Total	100.38	99.99	99.85	101.21	100.41	101.27	99.14	98.67	100.30	99.44	98.59	99.32	99.22	99.00	100.81
Si	0.984	0.988	0.986	0.980	0.989	0.987	0.983	0.962	0.986	0.964	0.972	1.000	0.991	0.979	0.978
<sup>27</sup> Al	0.016	0.012	0.014	0.020	0.011	0.013	0.017	0.026	0.014	0.036	0.028	0.000	0.009	0.021	0.022
<sup>26</sup> Al	0.019	0.015	0.012	0.003	0.017	0.002	0.010	0.000	0.012	0.016	0.016	0.016	0.014	0.002	0.014
Ti	0.001	0.002	0.001	0.001	0.001	0.001	0.001	0.000	0.001	0.001	0.000	0.000	0.000	0.002	0.001
Fe <sup>3+</sup>	0.000	0.000	0.000	0.016	0.001	0.011	0.000	0.001	0.003	0.018	0.014	0.000	0.001	0.015	0.010
Cr	0.000	0.000	0.000	0.000	0.001	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.001	0.000
Mg	0.494	0.506	0.444	0.504	0.572	0.550	0.573	0.588	0.537	0.568	0.615	0.163	0.606	0.648	0.583
Fe <sup>2+</sup>	0.465	0.453	0.520	0.450	0.388	0.423	0.370	0.374	0.416	0.370	0.332	0.813	0.349	0.304	0.379
Mn	0.008	0.013	0.015	0.016	0.012	0.006	0.010	0.012	0.015	0.012	0.011	0.006	0.013	0.007	0.005
Ca	0.012	0.011	0.009	0.011	0.008	0.007	0.026	0.010	0.016	0.013	0.010	0.004	0.021	0.020	0.008
Na	0.001	0.000	0.000	0.000	0.000	0.001	0.002	0.000	0.001	0.001	0.002	0.001	0.001	0.001	0.002

Note: Pyroxenes normalized to 2 cations. Fe<sup>3+</sup> calculated assuming 3 oxygens.

Experiments longer than 2 h were placed in evacuated Vycor tubes and run in a horizontal furnace. The sample end of the tube was immersed in water during sealing to prevent the sample from becoming heated prematurely. A 15-cm coil of 0.009-in. (0.023-cm) Fe wire was placed in each tube as an oxygen getter to maintain oxygen fugacity near the iron-wüstite or iron-magnetite buffers. This wire was separated from the pyroxene to prevent heterogeneous reaction. Ganguly (1982, pers. comm.) noted that the kinetics of experiments performed in a vacuum may be significantly faster than similar experiments performed at 1 atm. No such effect was observed in our results, however, suggesting that in this case the magnitude of this effect is smaller than the errors in our measurements.

Disordered starting materials were prepared by heating 2 g of each sample for 2 h at 900 °C. When held at lower temperatures during the subsequent experiments, this material became progressively more ordered. An additional portion of each sample was not disordered before it was sealed in Vycor tubes and run for the same length of time as the longest ordering experiment. These samples became disordered during the experiment and served as reversals to bracket the position of the equilibrium ordering state.

#### Mössbauer analysis

The ordering state of the experimental materials was obtained using Mössbauer spectroscopy in W. R. Dunham and R. H. Sands's laboratory at the Institute for Science and Technology at the University of Michigan. The details of the equipment and data reduction have been described elsewhere (Dunham et al., 1977; L. M. Anovitz, W. W. Zhao, and W. R. Dunham, in prep.) and will only be summarized here.

Approximately half of each run was ground to a powder and pressed at approximately 350 bars between layers of Baker reagent-grade boric acid in a 7-mm pellet press. Samples were cooled using liquid N<sub>2</sub> to 125 K during the Mössbauer run in order to enhance the M1/M2 splitting (Virgo and Hafner, 1969), and spectra were taken using a 35 mCi <sup>57</sup>Co in 6-μm Rh source and a velocity scan range of 8.00 mm/s. Data were collected on 1024 channels of a Tracor Northern Econ 1A multichannel ana-

lyzer with an NS 458 multiplexer. Most samples were run 2 to 4 h, with more important samples run overnight (8 to 12 h). The relatively short run times were made possible by the sensitivity of the equipment and data-reduction procedure, which was originally designed for low-Fe proteins. Calibrations of an absorption coefficient and the Debye temperature were obtained using the method of Anovitz et al. (in prep.).

Reduced spectra (Tables 2, 3, 4) were fitted to three quadrupole pairs: Fe<sup>2+</sup> in the M1 and M2 sites and Fe<sup>3+</sup> in the M1 site. Attempts to fit for Fe<sup>3+</sup> in the tetrahedral site gave results that were smaller than background in all samples tested. Spectroscopic data summarized by Rossman (1980) suggest that Fe<sup>3+</sup> is not present in the M2 site in orthopyroxenes. As the Fe<sup>3+</sup> contents of all of the samples studied here are quite small, we have assumed for the purpose of this study that no Fe<sup>3+</sup> is present in the M2 site. Results for Fe<sup>3+</sup> in M1 vary from 0% to 6.5% for the experimental run products. This scatter is probably due to noise, and a value of 2% ± 2% is reasonable for most of the experimental and natural samples studied. Electron-microprobe analyses (Table 1) yield Fe<sup>3+</sup> values of 0% to 1.8%. This is in reasonable agreement with the Mössbauer results.

For six peaks, a maximum of 18 variables may be fitted: the intensity, width, and position of each peak. Such a large number of variables would, however, force the program to fit background noise, and several constraints were imposed to reduce the number of fitted variables. The width of all peaks (full width at half height) was constrained to be equal. For M32b and PX4 where a large number of samples of the same material were analyzed, each spectrum was fitted, and the value of the width that minimized the "goodness-of-fit" parameter psi-squared (Dunham et al., 1977) was obtained. The average width for all spectra for each sample was then obtained, and all samples were refitted using this value. For materials where only one spectrum was run, the value of the width that minimized psi-squared was used. Several tests were made to determine if the constraint imposed on the peak width affected the resultant M1/M2 ratios. No significant deviation was found for any of the spectra tested.

An additional constraint was imposed by fixing the positions of the peaks for Fe<sup>3+</sup> in the M1 site at values determined by

TABLE 2. Results of Mössbauer analyses for sample M32b

Time (s)	M1		M2		M2		M1		Fe <sup>3+</sup> Int	X <sub>Fe<sup>1</sup></sub> <sup>M1</sup>	X <sub>Fe<sup>2</sup></sub> <sup>M2</sup>
	Vel	Int	Vel	Int	Vel	Int	Vel	Int			
500 °C											
300	-0.341	0.132	0.064	0.387	2.199	0.318	2.648	0.153	0.010	0.224	0.552
3634	-0.346	0.123	0.054	0.383	2.167	0.295	2.626	0.149	0.050	0.222	0.554
21 170	-0.338	0.128	0.059	0.391	2.175	0.302	2.631	0.152	0.027	0.223	0.553
42 391	-0.339	0.116	0.053	0.389	2.171	0.280	2.628	0.150	0.065	0.220	0.556
85 400	-0.347	0.125	0.066	0.404	2.178	0.315	2.624	0.144	0.012	0.212	0.564
258 470	-0.349	0.127	0.065	0.393	2.186	0.316	2.634	0.149	0.015	0.218	0.558
776 512	-0.362	0.110	0.063	0.427	2.171	0.318	2.613	0.136	0.010	0.192	0.584
1 210 945	-0.328	0.113	0.070	0.414	2.181	0.322	2.620	0.123	0.028	0.189	0.587
3 989 881	-0.357	0.096	0.061	0.424	2.182	0.342	2.626	0.109	0.029	0.164	0.612
3 989 871*	-0.326	0.066	0.058	0.477	2.180	0.368	2.592	0.080	0.010	0.114	0.662
600 °C											
300	-0.342	0.126	0.065	0.395	2.185	0.315	2.637	0.154	0.010	0.220	0.556
1 800	-0.346	0.119	0.063	0.401	2.175	0.317	2.626	0.142	0.017	0.207	0.569
3 600	-0.314	0.120	0.058	0.406	2.184	0.325	2.624	0.135	0.015	0.200	0.576
21 243	-0.323	0.103	0.072	0.424	2.184	0.325	2.625	0.119	0.029	0.178	0.598
42 344	-0.310	0.096	0.089	0.436	2.209	0.340	2.651	0.114	0.014	0.165	0.611
85 758	-0.344	0.096	0.063	0.429	2.181	0.338	2.617	0.117	0.020	0.169	0.607
258 270	-0.376	0.097	0.042	0.433	2.173	0.333	2.608	0.113	0.023	0.167	0.609
776 372	-0.357	0.100	0.068	0.425	2.191	0.343	2.633	0.109	0.023	0.166	0.610
3 989 650	-0.351	0.093	0.059	0.438	2.163	0.340	2.634	0.111	0.018	0.160	0.616
3 989 758*	-0.342	0.091	0.065	0.435	2.176	0.341	2.622	0.111	0.021	0.161	0.615
700 °C											
300	-0.347	0.109	0.065	0.412	2.181	0.315	2.622	0.146	0.018	0.200	0.576
600	-0.342	0.113	0.059	0.416	2.169	0.319	2.585	0.136	0.017	0.196	0.580
1 818	-0.310	0.108	0.087	0.404	2.181	0.336	2.642	0.142	0.010	0.196	0.580
3 600	-0.310	0.099	0.067	0.417	2.174	0.345	2.602	0.129	0.010	0.178	0.598
21 273	-0.340	0.102	0.059	0.428	2.178	0.329	2.626	0.129	0.013	0.182	0.594
42 334	-0.340	0.110	0.064	0.414	2.182	0.330	2.631	0.127	0.020	0.187	0.589
85 838	-0.352	0.104	0.065	0.413	2.182	0.322	2.621	0.118	0.044	0.180	0.596
776 557	-0.333	0.103	0.063	0.410	2.184	0.314	2.620	0.126	0.047	0.186	0.590
3 989 776	-0.343	0.109	0.064	0.408	2.176	0.329	2.627	0.125	0.029	0.187	0.589
3 989 881*	-0.333	0.104	0.067	0.416	2.179	0.323	2.625	0.134	0.023	0.189	0.587
800 °C											
300	-0.355	0.122	0.065	0.415	2.183	0.313	2.633	0.140	0.010	0.205	0.571
600	-0.333	0.122	0.061	0.412	2.166	0.317	2.607	0.149	0.000	0.210	0.566
1 200	-0.338	0.108	0.066	0.406	2.188	0.310	2.626	0.151	0.025	0.207	0.569
2 400	-0.327	0.114	0.064	0.403	2.160	0.321	2.604	0.153	0.010	0.209	0.567
3 600	-0.350	0.108	0.062	0.414	2.178	0.309	2.628	0.153	0.010	0.205	0.571
42 304	-0.331	0.116	0.066	0.398	2.182	0.309	2.614	0.141	0.035	0.207	0.569
85 884	-0.338	0.123	0.032	0.407	2.185	0.322	2.626	0.138	0.010	0.204	0.572
776 607	-0.341	0.121	0.070	0.402	2.182	0.314	2.629	0.143	0.020	0.204	0.572
3 989 863	-0.356	0.119	0.062	0.406	2.179	0.316	2.624	0.139	0.020	0.204	0.572
3 989 981*	-0.370	0.159	0.066	0.367	2.187	0.288	2.658	0.170	0.016	0.259	0.517
900 °C											
7 200*	-0.341	0.128	0.069	0.395	2.180	0.314	2.629	0.153	0.010	0.220	0.556

Note: Velocities are in mm/s relative to an Fe-foil standard; intensities are normalized to 1.0. Intensity for Fe<sup>3+</sup> represents the sum of the areas of both peaks in the doublet.

\* Disorder run.

Rossman (1980). As the intensities of these peaks were quite weak, a fit was obtained by first fixing the  $X_{Fe^1}^{M1}$ , intensities at zero and fitting  $X_{Fe^2}^{M1}$ , and  $X_{Fe^2}^{M2}$ . The intensities of  $X_{Fe^1}^{M2}$  were then fit to the residuals with  $X_{Fe^1}^{M1}$ , and  $X_{Fe^2}^{M2}$  held fixed.

Spectra for several samples of M32b and PX4-TM2 were repeated in order to evaluate the precision of the data set. Although many samples gave very similar ( $\pm 0.001 X_{Fe^1}^{M1}$ ) results in both runs, an average precision for  $X_{Fe^1}^{M1}$  of  $\pm 0.005$  for M32b and  $\pm 0.008$  for PX4-TM2 was obtained.

An example of the spectra obtained was fitted using the average width (0.16 mm/s) determined for sample PX4-TM2 (Fig. 2). The height of the fitted spectrum is less than that obtained by the most intense points in the spectrum, suggesting that the real line width was somewhat smaller than that shown for this sample. Tests of the effect of changes in the width parameter on the  $X_{Fe^1}^{M1}/X_{Fe^2}^{M2}$  ratio suggest that this small misfit will make little

or no difference in the result obtained. The background noise level in this spectrum is quite low. Much of the sinusoidal variation present is an artifact of baseline fitting and truncation processes in Fourier space during data reduction (Dunham et al., 1977; Anovitz et al., in prep.) and does not affect the fit.

An additional test was run using sample PX4-TM2 to test for possible errors due to quenching rate. Three samples, each ordered at 800 °C for 1 h, were quenched in different ways. One sample was quenched in liquid N<sub>2</sub> as was done with the remainder of the experiments in this study. A second sample was quenched using water in place of liquid N<sub>2</sub>, and the third by removing the sample and its support rod from the furnace by hand and leaving it on the lab bench to cool. These runs yielded  $X_{Fe^1}^{M1}$  values of 0.729, 0.729, and 0.728, respectively, well within the analytical precision, and it was concluded that quenching in liquid N<sub>2</sub> is sufficiently rapid that cation ordering during quench-

TABLE 3. Results of Mössbauer analyses for sample PX4-TM2

Time (s)	M1		M2		M2		M1		Fe <sup>3+</sup>	X <sub>Fe</sub> <sup>M1</sup>	X <sub>Fe</sub> <sup>M2</sup>
	Vel	Int	Vel	Int	Vel	Int	Vel	Int			
500 °C											
300	-0.374	0.198	0.105	0.303	2.123	0.243	2.678	0.246	0.010	0.729	0.897
3600	-0.375	0.204	0.102	0.304	2.113	0.239	2.670	0.243	0.010	0.735	0.891
21373	-0.367	0.197	0.119	0.302	2.126	0.234	2.673	0.240	0.026	0.731	0.895
42709	-0.373	0.196	0.106	0.299	2.126	0.243	2.678	0.238	0.025	0.722	0.904
86170	-0.336	0.189	0.109	0.305	2.131	0.236	2.676	0.235	0.036	0.714	0.912
259260	-0.370	0.198	0.103	0.298	2.128	0.249	2.677	0.242	0.013	0.724	0.902
776997	-0.372	0.192	0.108	0.310	2.124	0.245	2.680	0.236	0.018	0.707	0.919
1212043	-0.363	0.196	0.105	0.302	2.132	0.250	2.685	0.235	0.018	0.712	0.914
3989761	-0.378	0.197	0.101	0.313	2.119	0.246	2.675	0.234	0.010	0.708	0.918
3989881*	-0.370	0.199	0.107	0.297	2.121	0.244	2.674	0.233	0.027	0.721	0.905
600 °C											
300	-0.373	0.205	0.100	0.294	2.123	0.242	2.680	0.236	0.024	0.735	0.891
1800	-0.372	0.192	0.102	0.309	2.123	0.239	2.669	0.238	0.021	0.715	0.911
3600	-0.377	0.198	0.101	0.296	2.122	0.244	2.677	0.241	0.020	0.729	0.897
21362	-0.374	0.196	0.111	0.312	2.113	0.243	2.683	0.248	0.000	0.723	0.903
42689	-0.369	0.202	0.103	0.296	2.119	0.249	2.678	0.235	0.017	0.724	0.902
86118	-0.352	0.205	0.123	0.297	2.144	0.260	2.691	0.238	0.000	0.720	0.906
259150	-0.377	0.193	0.093	0.316	2.065	0.241	2.659	0.240	0.009	0.710	0.916
776822	-0.380	0.199	0.103	0.318	2.119	0.244	2.668	0.239	0.000	0.712	0.914
3989685	-0.379	0.198	0.096	0.308	2.121	0.238	2.675	0.238	0.018	0.721	0.905
3989806*	-0.368	0.194	0.103	0.301	2.117	0.237	2.672	0.238	0.030	0.724	0.902
700 °C											
300	-0.381	0.197	0.104	0.296	2.119	0.239	2.673	0.250	0.018	0.741	0.885
600	-0.375	0.206	0.091	0.296	2.118	0.245	2.670	0.237	0.016	0.732	0.894
1800	-0.380	0.196	0.100	0.301	2.124	0.247	2.675	0.241	0.015	0.722	0.904
3600	-0.374	0.194	0.102	0.300	2.126	0.235	2.679	0.237	0.034	0.725	0.901
21287	-0.371	0.208	0.101	0.295	2.116	0.244	2.669	0.232	0.021	0.731	0.895
42529	-0.367	0.195	0.102	0.302	2.128	0.247	2.672	0.233	0.023	0.713	0.913
86050	-0.368	0.198	0.100	0.300	2.125	0.240	2.672	0.236	0.026	0.724	0.902
776717	-0.371	0.197	0.105	0.301	2.118	0.249	2.672	0.244	0.010	0.723	0.903
3989661	-0.368	0.183	0.104	0.296	2.126	0.226	2.677	0.227	0.067	0.716	0.910
3989771*	-0.371	0.196	0.097	0.303	2.114	0.242	2.665	0.243	0.016	0.725	0.901
800 °C											
291	-0.370	0.200	0.109	0.302	2.134	0.245	2.687	0.237	0.016	0.722	0.904
603	-0.369	0.203	0.100	0.303	2.113	0.241	2.668	0.244	0.010	0.734	0.892
1221	-0.370	0.200	0.100	0.302	2.120	0.234	2.674	0.242	0.016	0.731	0.895
2400	-0.379	0.198	0.093	0.298	2.170	0.233	2.743	0.239	0.031	0.735	0.891
3636**	-0.375	0.196	0.102	0.295	2.118	0.238	2.666	0.238	0.033	0.730	0.896
3845†	-0.382	0.200	0.097	0.305	2.115	0.241	2.667	0.245	0.010	0.730	0.896
3602‡	-0.329	0.200	0.153	0.305	2.198	0.237	2.769	0.239	0.020	0.728	0.898
42485	-0.367	0.191	0.105	0.299	2.121	0.235	2.678	0.247	0.029	0.732	0.894
86080	-0.372	0.197	0.100	0.306	2.117	0.247	2.669	0.249	0.000	0.726	0.900
776732	-0.383	0.197	0.104	0.304	2.125	0.243	2.676	0.241	0.016	0.723	0.903
3989753	-0.382	0.230	0.107	0.281	2.130	0.209	2.685	0.280	0.000	0.830	0.796
3989910*	-0.389	0.239	0.101	0.264	2.115	0.210	2.677	0.288	0.000	0.856	0.770
900 °C											
7200*	-0.371	0.200	0.100	0.301	2.111	0.232	2.665	0.242	0.025	0.738	0.889

Note: Velocities are in mm/s relative to an Fe-foil standard; intensities are normalized to 1.0. Intensity for Fe<sup>3+</sup> represents the sum of the areas of both peaks of the doublet.

\* Disordering run.

\*\* Liquid N<sub>2</sub>-quench test run.

† Water-quench test run.

‡ Air-quench test run.

ing is not a problem for experiments at temperatures less than 800 °C.

EXPERIMENTAL RESULTS

Figures 3 and 4 show the experimental results plotted as a function of time. Both samples showed clear changes as a function of time and temperature. At 800 °C, equilibrium was reached in less than the minimum experimental run time (5 min) for both samples. Progressive changes toward equilibrium were observed at 500, 600, and 700 °C, although equilibrium was not achieved at

500 °C. Because of the high bulk Fe content in PX4-TM2, the range of possible X<sub>Fe</sub><sup>M1</sup> values is smaller and the error brackets are larger than for M32b. At long run times some of the PX4-TM2 runs gave anomalous results. As orthopyroxene of this composition is metastable at 1 atm relative to olivine and quartz (Lindsley, 1983), material from these runs was X-rayed to test for possible reaction during the experiment. No olivine, quartz, or magnetite was observed by either optical or X-ray means, however, and the cause of the changes in these runs remains unexplained.

TABLE 4. Results of Mössbauer analyses for natural samples

Sample no.	M1		M2		M2		M1		Fe <sup>3+</sup> Int	X <sub>Fe<sup>3+</sup></sub> <sup>M1</sup>	X <sub>Fe<sup>3+</sup></sub> <sup>M2</sup>
	Vel	Int	Vel	Int	Vel	Int	Vel	Int			
PX4-TM2	-0.367	0.186	0.116	0.329	2.136	0.243	2.694	0.220	0.023	0.675	0.951
M32B	-0.346	0.031	0.062	0.517	2.192	0.405	2.576	0.036	0.010	0.053	0.723
RIV83C 22	-0.362	0.042	0.060	0.514	2.177	0.396	2.615	0.038	0.010	0.051	0.587
PSO83C 8	-0.339	0.032	0.061	0.510	2.193	0.408	2.639	0.040	0.010	0.050	0.641
SAG80 3	-0.515	0.024	0.038	0.511	2.177	0.396	2.570	0.042	0.026	0.053	0.727
HUT83C 9	-0.258	0.045	0.062	0.515	2.184	0.407	2.500	0.032	0.000	0.059	0.692
HAL84B 40	-0.302	0.040	0.058	0.512	2.172	0.402	2.494	0.037	0.010	0.057	0.684
GRU83C 15	-0.218	0.059	0.062	0.492	2.176	0.391	2.440	0.033	0.025	0.074	0.705
ALG83C 10	-0.407	0.048	0.054	0.476	2.181	0.375	2.663	0.056	0.046	0.099	0.807
M20B	-0.310	0.078	0.074	0.476	2.167	0.363	2.616	0.084	0.000	0.135	0.702
REN84B 7	-0.355	0.035	0.040	0.485	2.167	0.392	2.600	0.063	0.025	0.070	0.629
A5B	-0.321	0.060	0.070	0.465	2.181	0.379	2.620	0.080	0.018	0.132	0.798
GRU84B 1	-0.328	0.055	0.068	0.475	2.162	0.389	2.585	0.061	0.020	0.103	0.765
BA9A	-0.284	0.072	0.080	0.492	2.179	0.358	2.627	0.077	0.066	0.140	0.792
BA7D	-0.313	0.071	0.071	0.448	2.149	0.369	2.563	0.076	0.037	0.158	0.882

Note: Velocity is in mm/s relative to an Fe-foil standard; intensities are normalized to 1.0. Intensity for Fe<sup>3+</sup> represents the sum of the areas of both peaks of the doublet.

Ln  $K_D$  vs.  $1/T$  curves for our data (Fig. 5) are distinctly different from those suggested by Ganguly (1982). The differences are relatively small at 800 and 900 °C, but increase with decreasing temperature. The positions of our curves relative to those of Ganguly (1982) imply that equilibrium temperatures calculated from our model will be substantially lower than his. A least-squares fit to the data yields

$$\ln K_D(\text{M32b}) = 2135.27/T - 0.3307 \quad (17)$$

$$\ln K_D(\text{PX4}) = 1291.83/T - 0.0554, \quad (18)$$

where  $T$  is in kelvins. If  $\ln K$  (Eq. 3) is modeled as a linear function of  $1/T$  (cf. Ganguly, 1982) Equations 17 and 18 can be combined with Equation 3 to solve for  $\ln K$  as a function of temperature (two coefficients) and the mixing parameters  $\bar{W}^{M1}$  and  $\bar{W}^{M2}$ . As Equations 17 and 18 are both linear, only four coefficients can be derived from these data, one of which must be the temperature dependence of  $\ln K$ ; and as we have chosen to use Equa-

tion 3 rather than Equation 4, our model thus does not explicitly solve for  $\Delta G$ . Solution of these equations yields (model 1)

$$\ln K = 1203.30/T + 0.1272, \quad (19)$$

where  $T$  is in kelvins, and

$$\bar{W}^{M1} = 5449 \text{ J/mol} \quad (20)$$

$$\bar{W}^{M2} = 2083 \text{ J/mol}. \quad (21)$$

The results of this fit (Fig. 1, solid line) are significantly less ordered than those suggested by Ganguly (1982, dashed line). The resultant curve is in reasonably good agreement with the preliminary results of Besancon, Spasato, and Grover (written comm.), which were not included in the fitting procedure.

Chatillon-Colinet et al. (1983) measured the enthalpy of solution along the join enstatite-ferrosilite and used their data to obtain a value for  $W_H$ , the bulk enthalpy of mixing of  $3970 \pm 850$  J per  $\text{MSiO}_3$  unit. They noted, without derivation that for this formula unit,  $W_H$  is equal to the average of  $\bar{W}^{M1}$  and  $\bar{W}^{M2}$ . Our data give an estimated value for  $W_H$  of 3770 J/mol, in remarkably good agreement with the data of Chatillon-Colinet et al. (1983). The experiments by Chatillon-Colinet et al. were carried out at 750 °C after a 2- to 3-h thermal equilibration time on experimental materials synthesized at 1120 °C, 20 kbar. Chatillon-Colinet et al. suggested that this may not be enough time for the ordering state of the sample to totally equilibrate. Our data, however, suggest that at 700 °C, approximately 1 h is sufficient for equilibrium to be obtained, and the samples of Chatillon-Colinet et al. probably represent measurements on materials with an equilibrium ordering state.

Similarly, our data may also be used to calculate the disordering enthalpy measured by Chatillon-Colinet et al. (1983). The data of Chatillon-Colinet et al. yield a disordering enthalpy of  $7100 \pm 3300$  J ( $1700 \pm 780$  cal) per  $\text{M}_2\text{Si}_2\text{O}_6$  formula unit between a natural and experimen-

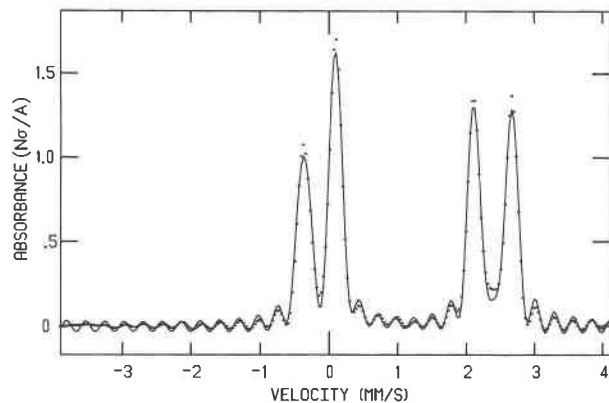


Fig. 2. Representative Mössbauer spectrum for orthopyroxene obtained during this study. The sinusoidal background is an artifact of the Fourier transform used in the data-reduction process, which has no effect on the fitting process.

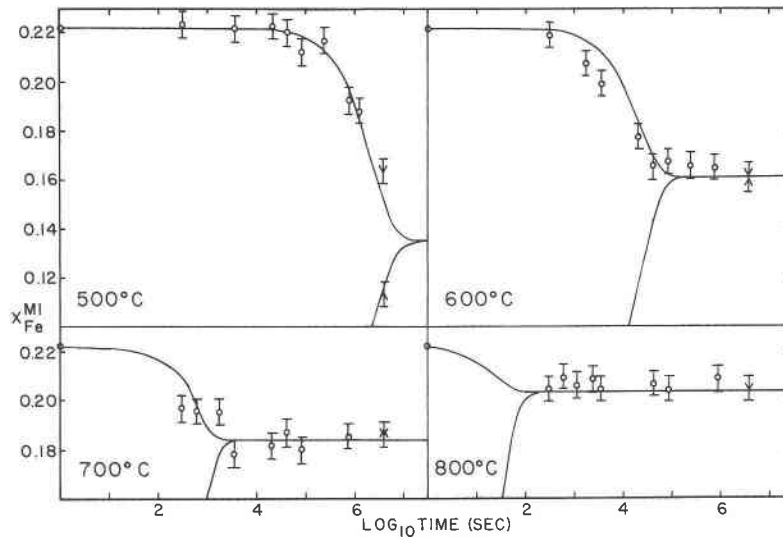


Fig. 3. Kinetic experiments for sample M32b showing experimentally attained values for  $X_{Fe}^{M1}$  and error brackets as a function of  $\log_{10} t$  (s). Solid lines show ordering and disordering paths calculated for this sample.

tally disordered pyroxene. Unfortunately, the ordering states of these materials were not measured. Using the ordering states estimated by Chatillon-Colinet et al. and Eq. 18 of Ganguly (1986), our model yields  $\Delta H^{dis} = 3347$  J (800 cal). The agreement between these results is marginal at best and suggests that further refinement is necessary before the thermodynamics of ordering in orthopyroxenes is well understood.

Alternatively, the data of Chatillon-Colinet et al. (1983) may be used as a further constraint that will allow all five unknowns to be determined. This analysis yields (model 2)

$$\ln K = 1203.30/T + 0.1272 \quad (22)$$

where  $T$  is in kelvins, and

$$\Delta G^* = 400.5 \text{ J/mol} \quad (23)$$

$$W^{M1} = 5649 \text{ J/mol} \quad (24)$$

$$W^{M2} = 2283 \text{ J/mol.} \quad (25)$$

Again, this analysis assumes that  $W^H$  may be taken as the average of  $W^{M1}$  and  $W^{M2}$ . The results for  $\ln K$  as a function of temperature,  $W^{M1}$  and  $W^{M2}$  are, as expected, very close to those from our first model, and  $\Delta G^*$  is close to zero. Data fit to Equation 4 have been modeled by Sack (1980) and Davidson and Lindsley (1985). As both data sets rely on the data of Saxena and Ghose (1971) and Besancon (1981a) and Sack and Davidson and Lindsley assumed that these experiments yielded equilibrium results rather than half-reversals, it is not surprising that our results disagree with previous models in that our reversed data yield a model that is significantly less ordered than has previously been suggested. Nonetheless, our results are within the general ranges suggested by Sack (1980) for all of the parameters involved. Although our model

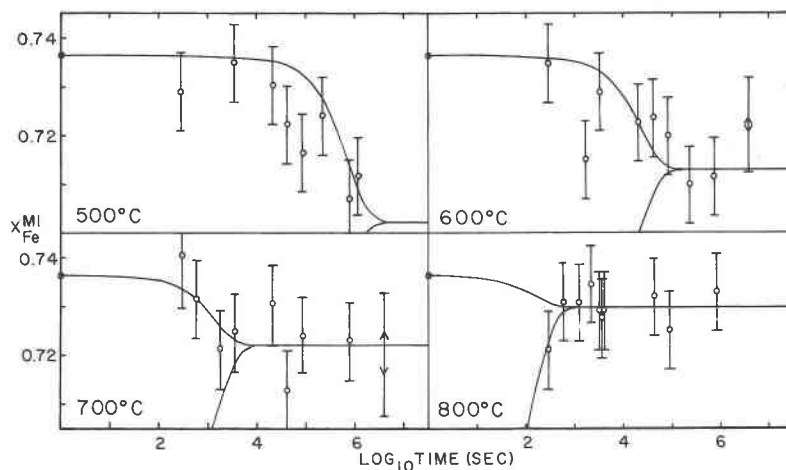


Fig. 4. Kinetic experiments for sample PX4-TM2 showing experimentally attained values for  $X_{Fe}^{M1}$  and error brackets as a function of  $\log_{10} t$  (s). Solid lines show ordering and disordering paths calculated for this sample at four temperatures.



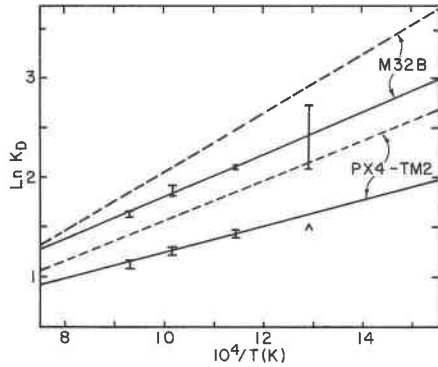


Fig. 5.  $\ln K_D$  vs.  $1/T$  ( $T$  in kelvins) for samples M32b and PX4-TM2. Dashed lines show the values predicted by the model of Ganguly (1982); solid lines are least-squares fits to our data (brackets).

2 yields values for all of the coefficients in Equation 4, the use of the more complex equation is not justified, as the simpler model 1 fits all of the data (including the data of Chatillon-Colinet et al., 1983) within error, and the remaining calculations in this paper were made with model 1.

Sharma et al. (1987) attempted to constrain the Gibbs energy of mixing for orthopyroxenes on the join enstatite-ferrosilite by direct measurement using electrochemistry at 1000 K. Unfortunately, the results from their experiments are in sharp disagreement with all other available experiments for this join, including our own, as they suggest a much greater degree of nonideality than all previous studies. The results of Sharma et al. yield an excess Gibbs energy of mixing of approximately  $1900 \pm 200$  J/mol for an orthopyroxene with  $X_{Fe} = 0.36$  (MSiO<sub>3</sub> formula unit). For sample M32b ( $X_{Fe} = 0.388$ ), our calculations yield an excess Gibbs energy of mixing of 565 J/mol, significantly less than the results of Sharma et al. (1987). As the results of Sharma et al. are significantly different from results obtained by all other workers on this system, we suspect that the data of Sharma et al. are in error. Sharma et al. annealed their samples at 1000 K for 12 h prior to the experiment. Our kinetic data suggest that it is unlikely that failure to reach an equilibrium ordering state is the cause of the discrepancy. The explanation of the observed discrepancy, however, must await careful re-examination of the electrochemistry of orthopyroxenes.

Having derived a model for equilibrium ordering in orthopyroxenes, the kinetic data may be reduced and fitted to a model for ordering rates as a function of temperature and composition. It is incorrect to obtain a value by calculating the rate constant  $C_0\tilde{K}$  for all experiments at one temperature and averaging the results. Runs in which no change occurred, or which reached equilibrium, yield only maximum or minimum rates, respectively. Least-squares analysis yields

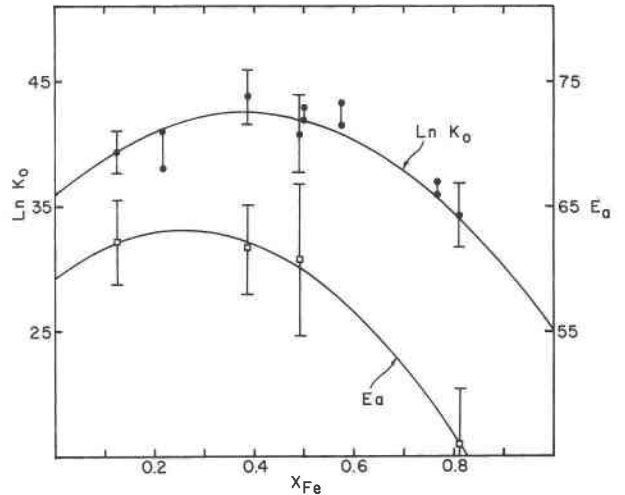


Fig. 6. Data and fitted model for  $\ln K_0$  and  $E_a$  as a function of  $X_{Fe}$  for orthopyroxene. Square brackets are the data of Besancon (1981a) and our own data to which the model was fitted. Dotted brackets for  $\ln K_0$  are calculated from the data of Virgo and Hafner (1969) and Domeneghetti et al. (1985) using the fitted  $E_a$  model and are included for comparison.

$$\ln C_0\tilde{K}(\text{M32b}) = -(31033 \pm 1800)/T + (26.543 \pm 2.2) (\pm 0.724 \text{ s}^{-1}) \quad (26)$$

$$\ln C_0\tilde{K}(\text{PX4}) = -(23141 \pm 2300)/T + (27.052 \pm 2.7), (\pm 0.911 \text{ s}^{-1}) \quad (27)$$

where  $T$  is in kelvins and the standard errors for each coefficient are given.

Besancon (1981a) experimentally disordered two samples, TZ ( $X_{Fe} = 0.492$ ) and HC ( $X_{Fe} = 0.129$ ). Refitting his data to obtain standard errors yields

$$\ln C_0\tilde{K}(\text{TZ}) = -(30578 \pm 3100)/T + (23.596 \pm 3.1) (\pm 0.724 \text{ s}^{-1}) \quad (28)$$

$$\ln C_0\tilde{K}(\text{HC}) = -(31281 \pm 1700)/T + (22.135 \pm 1.7), (\pm 0.911 \text{ s}^{-1}) \quad (29)$$

Calculations using the X-ray compositions of Domeneghetti et al. (1985) yield the following ranges of results:  $\ln C_0\tilde{K} = -9.014$  to  $-11.530$  (sample 274,  $X_{Fe} = 0.218$ ),  $\ln C_0\tilde{K} = -5.536$  to  $-6.286$  (sample 10,  $X_{Fe} = 0.494$ ), and  $\ln C_0\tilde{K} = -5.574$  to  $-6.383$  (sample 10/68,  $X_{Fe} = 0.768$ ).

Virgo and Hafner (1969) experimentally disordered sample 3209 at 500 and 1000 °C. Ganguly (1982) noted, however, that their 1000 °C experiments appear to have reset during cooling and should not be used. Their 500 °C data yield  $\ln C_0\tilde{K}(X_{Fe} = 0.574) = -11.596$  to  $-13.135$ .

The data presented above show a strong, nonlinear dependence on composition for both the pre-exponential factor ( $K_0$ ) and the activation energy ( $E_a$ ). Our data and that of Besancon (1981a) (Fig. 6) yield four data points

for  $K_0$  and  $E_a$  as a function of composition, which have been fit to three-term polynomials, yielding

$$\ln K_0 = (35.875 \pm 3.1) + (35.05 \pm 14.7)X_{\text{Fe}} - (45.70 \pm 1.7)X_{\text{Fe}}^2 \quad (\pm 1.698 \text{ yr}^{-1}) \quad (30)$$

$$E_a = (59150 \pm 1600) + (30170 \pm 7500)X_{\text{Fe}} - (56900 \pm 7600)X_{\text{Fe}}^2 \quad (\pm 863 \text{ cal}) \quad (31)$$

where  $\ln C_0 \vec{K} = \ln K_0 - E_a/RT$  and  $T$  is in kelvins. It is unclear whether the drop at high Fe contents is real or due to errors in the PX4-TM2 data. It is also possible that part of the observed variation is due to small percentages of Al or  $\text{Fe}^{3+}$  in the samples studied. Further work on high-Fe, aluminous, and oxidized orthopyroxenes will be necessary to clarify this point.

The data of Virgo and Hafner (1969) and Domeneghetti et al. (1985) have not been included in these fits, as  $E_a$  values cannot be calculated from single-temperature data sets. The experiments of Domeneghetti et al. (1985) were only done at one temperature and therefore cannot be fitted to a temperature-dependent model. In addition, the discrepancy between their microprobe analyses (EDA) and the Fe content of their samples derived from the single-crystal refinement makes their data suspect. Their data may, however, be compared to the fitted results by using the  $E_a$  values fitted to the other experiments to calculate  $K_0$ . The brackets shown for their data (dotted brackets, Fig. 6) are not true error brackets, but simply represent the range of values obtained from the data. The results obtained are close to the fitted curve, but are slightly lower at small  $X_{\text{Fe}}$  and slightly higher at high  $X_{\text{Fe}}$ . As these values are based on  $E_a$  values estimated from our model, these data have not been included in the fit, but the close agreement suggests that the model is reasonable.

## APPLICATIONS

The goal of this study was to test whether the extremely rapid cooling rates obtained using the orthopyroxene geospeedometer on granulite-facies pyroxenes were artifacts of errors in the available equilibrium and kinetic data. Having derived our model, the first test of its applicability is to obtain cooling rates for the experimental samples. These calculations will be free of errors due to differing bulk compositions. All cooling rate calculations were made using the program CLRATE provided by J. Ganguly, which solves for the cooling rates as described above. Sample PX4-TM2 has been excluded from this analysis, as its unknown provenance makes interpretation of results impossible.

Calculated closure and quenching temperatures and cooling rates for M32b, Besancon's sample TZ, and several other natural samples are listed in Table 5. As the choice of cooling model is relatively arbitrary, we have used the asymptotic model (Eq. 16). Test calculations suggest that calculated linear cooling rates obtained from the two models are similar. Results for both M32b and

TZ are encouraging. Sample M32b yields a value for  $T_c$  of 510 K and a cooling rate of 12 °C/m.y. (or 2.2 °C/m.y. using the compositionally dependent kinetic model), and TZ yields 470 K and 0.001 °C/m.y. using Besancon's kinetic data (or 0.1 °C/m.y. with our compositionally dependent model). These results are orders of magnitude slower than those obtained previously (Besancon, 1981b; Ganguly, 1982; Saxena and Dal Negro, 1983) and within the range expected from geophysical and isotopic studies.

The results for all of the samples processed are likewise much improved over previous results. Saxena and Dal Negro (1983) obtained cooling rates for 10 natural samples from granulite terranes analyzed by Virgo and Hafner (1970). Their results ranged from 0.1 to 20 °C/yr. For these same data, our calculations (Table 5) yield cooling rates in the range 0.1 to 100 °C/m.y. for 7 of the 10 samples. Overall, 41 of 85 samples yield cooling rates in this range. Although calculated cooling rates display considerable scatter (Figs. 7 and 8), reasonable cooling rates are now obtained for granulite-facies terranes from studies of ordering in orthopyroxenes.

Some of the scatter may be due to contamination of the samples. In our own work we found that several of the natural samples showed additional Mössbauer peaks that interfered with the M1 peaks, probably because of amphibole or clinopyroxene. Such interference was not a problem in our experimental materials. Correction of the results for these interferences often significantly lowered the calculated equilibrium temperature.

Virgo and Hafner (1970) also measured octahedral ordering states for several orthopyroxenes derived from igneous rocks. Four of these samples (HK) are from dacites in Japan, one is from an andesite from the island of Dominica (DOM 1), and one is from the Stillwater Complex, Montana (N5). Cooling rates for these samples have been calculated assuming an initial temperature of 1000 °C. The calculated equilibrium temperature (260 °C) for the Stillwater sample is quite low relative to those for the volcanic samples, which suggests that the calculated cooling rate (0.13 °C per 10<sup>3</sup> yr) is averaged over nearly the entire cooling history of the pluton. This averaging may account for the relatively slow rate obtained. The results from the volcanic samples seem reasonable (63 °C/d to 330 °C/yr), but without more detailed information on the sample location, the significance of the results cannot be evaluated.

## SOURCES OF ERROR

Several sources of error exist that may account for the observed scatter in the calculated cooling rates. These include errors in the chemical analyses and Mössbauer data, solid-solution effects, and imprecisions in the equilibrium and kinetic models.

Plots of temperature and cooling rate as a function of composition (Figs. 7 and 8) may be used to test for non-random errors imposed by inadequacies in our compo-

TABLE 5. Equilibrium temperatures and cooling rates calculated for natural samples

Sample	Ref.	Fe	Ca	Al	$X_{Fe}^{M2}$	$T_c$ (K)	$T_o$ (K)	$\eta_{(asym)}$ ( $K^{-1} \cdot yr^{-1}$ )	$dT/dt$
Samples from granulite-facies metamorphic rocks									
O-1	1, 3	0.577	0.018	0.031	0.876	605	560	0.1953E-06	0.117*
O-4	1, 3	0.475	0.019	0.020	0.822	558	510	0.4768E-09	260**
4642A	1, 3	0.578	0.013	0.025	0.910	526	510	0.1250E-09	68.4**
R1742	1, 3	0.576	0.012	0.025	0.908	529	485	0.1455E-09	75.7**
CH113	1, 3	0.483	0.009	0.020	0.853	511	485	0.4768E-11	2.48**
68671	1, 3	0.531	0.013	0.025	0.899	499	460	0.4219E-11	2.08**
37218	1, 3	0.531	0.048	0.031	0.869	560	510	0.1953E-08	1070**
7286	1, 3	0.496	0.016	0.026	0.869	504	485	0.1250E-10	6.51**
277	1, 3	0.430	0.010	NAD	0.797	489	458	0.4219E-12	0.207**
355	1	0.766	0.009	0.026	0.928	638	560	0.6939E-05	4.17*
XYZ	1	0.877	0.019	0.019	0.970	517	463	0.4219E-11	2570**
276	1	0.738	0.011	NAD	0.927	610	540	0.9313E-06	0.540*
207	1	0.705	0.016	NAD	0.900	685	610	0.1164E-03	76.2*
Bl-9	1	0.698	NAD	NAD	0.899	680	653	0.5960E-04	41.8*
205	1	0.625	0.017	NAD	0.886	635	560	0.3164E-05	1.90*
278	1	0.623	0.013	NAD	0.905	580	535	0.3815E-07	2190**
264	1	0.591	0.013	NAD	0.920	515	485	0.7451E-10	38.8**
277	1	0.442	0.010	NAD	0.797	527	460	0.1562E-10	7.71**
274	1	0.172	0.005	NAD	0.322	596	535	0.3815E-09	219**
V2	1	0.758	0.020	0.009	0.922	658	560	0.3309E-04	19.9*
3209	1	0.574	0.020	0.022	0.922	552	510	0.1819E-08	995**
R96	1	0.430	0.016	0.090	0.897	591	548	0.1694E-07	9960**
37651	1	0.406	0.010	0.023	0.754	523	460	0.1780E-10	8.79**
SP18	1	0.400	0.005	0.059	0.747	539	510	0.3052E-10	16.7**
115/3	1	0.390	0.012	0.058	0.732	541	485	0.2441E-10	12.7**
A	1	0.386	0.008	0.046	0.716	464	428	0.1335E-13	0.006**
274	2	0.218	0.006	0.000	0.735	490	485	0.2378E-12	0.124**
10	2	0.494	0.014	0.002	0.868	502	460	0.4224E-11	2.08**
10/68	2	0.767	0.018	0.000	0.767	413	403	0.1001E-12	0.043**
37218	4	0.531	0.020	0.050	0.900	497	460	0.4219E-11	2.08**
TZ	3, 5	0.496	0.014	0.037	0.888	467	338	0.2373E-12	0.112**
HC	5	0.128	0.010	0.021	0.830	748	635	0.6939E-05	4.73**
M32b	6	0.388	0.013	0.052	0.723	511	485	0.4219E-11	2.20**
RIV 83C 22	6	0.319	0.020	0.023	0.587	584	510	0.7451E-09	408**
PSO 83C 8	6	0.346	0.010	0.044	0.663	550	510	0.4768E-10	26.1**
SAG 80 3	6	0.389	0.008	0.036	0.725	511	483	0.3168E-11	1.64**
HUT 83 C9	6	0.375	0.010	0.026	0.692	543	483	0.2241E-10	11.6**
HAL 84B 40	6	0.371	0.026	0.027	0.684	544	483	0.3052E-10	15.8**
GRU 83C 15	6	0.390	0.008	0.028	0.705	570	518	0.4441E-09	247**
ALG 83C 10	6	0.453	0.011	0.027	0.807	536	483	0.9313E-10	48.3**
M20B	6	0.419	0.016	0.026	0.702	689	623	0.1355E-04	9.06*
REN 84B 7	6	0.350	0.021	0.023	0.629	613	560	0.1355E-07	8140**
A5B	6	0.465	0.012	0.035	0.798	586	510	0.5551E-08	3040**
GRU 84B 1	6	0.434	0.007	0.015	0.764	577	535	0.2842E-08	1630**
BA9A	6	0.466	0.011	0.023	0.791	602	518	0.2647E-07	0.015*
BA7D	6	0.520	0.009	0.026	0.882	517	483	0.3164E-10	16.4**
Igneous samples									
HK52110301	1	0.569	0.018	0.006	0.800	810	733	0.2441E-01	62.4†
HK56071001	1	0.534	0.004	0.014	0.804	721	658	0.2373E-03	199*
HK53051501	1	0.491	0.014	0.033	0.788	670	603	0.7500E-05	5.76*
HK53051602	1	0.462	0.027	0.034	0.734	739	660	0.4163E-03	350*
DOM1	1	0.457	0.023	0.008	0.725	750	585	0.4441E-03	331*
N5	1	0.272	0.031	0.023	0.506	579	535	0.1953E-09	133**

Note: References are (1) Virgo and Hafner (1970), (2) Domenegetti et al. (1985), (3) Saxena and Dal Negro (1983), (4) Ghose (1965), (5) Besancon (1981a), and (6) this study. NAD = no analytical data available.

\* °C/yr. \*\* °C/m.y. † °C/d.

sitional models or measurement techniques. There is a wide scatter in equilibrium temperature and cooling rate as a function of composition. This scatter appears to be essentially random below  $X_{Fe} = 0.5$ . At higher Fe contents, both temperature and cooling rate appear to increase with increasing Fe content. This increase may simply reflect errors in the  $X_{Fe}^{M2}/X_{Fe}^{M1}$  ratio. There are several additional factors that may have affected these results. One sample that yields a reasonable cooling rate was

measured by single-crystal X-ray diffraction (Domenegetti et al., 1985). As the relative peak ratios become closer to one, small errors in measured peak areas become relatively more important because the change in the equilibrium ordering state as a function of temperature becomes smaller. Small errors in measured peak areas also become more important as the ratios approach zero (or infinity). The bias in the results obtained from the Fe-rich samples toward higher temperatures (larger  $X_{Fe}^{M1}$  val-

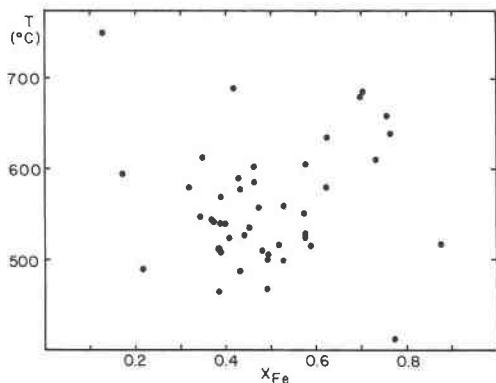


Fig. 7. Closure temperature  $T_c$  as a function of composition obtained for the granulite-facies natural orthopyroxenes from our own work and the literature listed in Table 5.

ues) suggests that this cannot be the total explanation, as measurement imprecision would tend to increase the scatter in the measured temperatures.

Imprecise measurements of  $X_{Fe}^{M1}$  may affect the results if significant amounts of  $Fe^{3+}$  are present in a sample. This effect should be more significant in single-crystal X-ray determinations than in Mössbauer studies. The X-ray cross sections for  $Fe^{3+}$  and  $Fe^{2+}$  are not sufficiently different for X-ray measurements to distinguish them. Thus single-crystal X-ray refinements tend to lump  $X_{Fe}^{M1}$  with  $X_{Fe}^{M2}$ , yielding erroneously high levels of disorder. In most Mössbauer studies, there is sufficient splitting between the  $Fe^{3+}$  and  $Fe^{2+}$  peaks that the peaks do not overlap, and small amounts of  $Fe^{3+}$  are lost in the noise. The low-velocity peak for  $Fe^{3+}$  in the M1 site in orthopyroxenes (approx. 0.235 mm/s, Rossman, 1980) is close enough to the low-velocity peak for  $Fe^{2+}$  in M2 (0.03 mm/s, Rossman, 1980) that depending on the line width and the data-reduction procedure, part of the  $Fe^{3+}$  may be incorrectly added to the M2 intensity. This would yield erroneously high levels of order. The high-Fe sample measured by Domeneghetti et al. (1985) using single-crystal X-ray techniques, however, yields anomalously high levels of ordering, and incorrect  $Fe^{3+}$  determinations cannot be the source of the discrepancy between this sample and the Mössbauer measurements of high-Fe orthopyroxenes.

Calculated cooling rates are strongly dependent on the precision of the chemical analysis and the method used to measure the partitioning (Ganguly, 1982; Saxena and Dal Negro, 1983). For sample M32b, a 1 mol% increase in measured Fe ( $X_{Fe} = 0.398$ ) decreases the calculated equilibrium temperature from 510 to 504 K and decreases the calculated cooling rate from 2.2 °C/m.y. (using the compositionally dependent kinetic model) to 0.83 °C/m.y. Similarly, increasing  $X_{Fe}^{M1}$  from 0.053 to 0.063 raises the equilibrium temperature to 541 K and increases the cooling rate to 94 °C/m.y.

The potential importance of measurement errors as a source of scatter in the calculated cooling rates may be

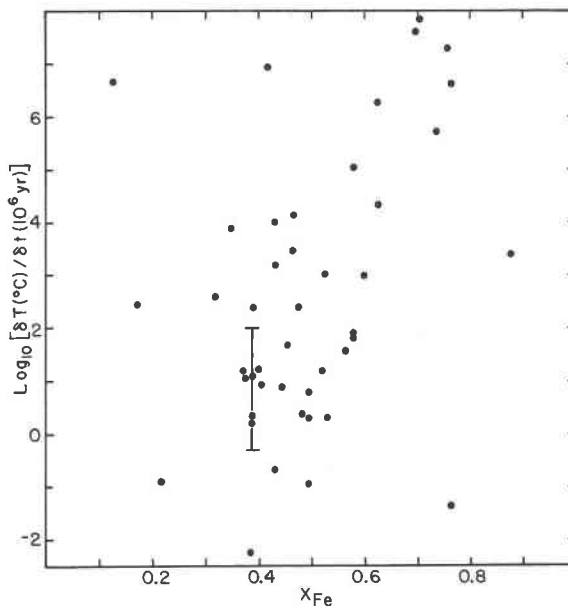


Fig. 8. Linear cooling rates as a function of composition obtained for the granulite-facies natural orthopyroxenes from our own work and the literature listed in Table 5.

evaluated by comparing results obtained in different laboratories on the same samples. For sample 37218 ( $X_{Fe} = 0.531$ ), Virgo and Hafner (1970) obtained a value for  $X_{Fe}^{M2}$  of 0.869 on the basis of low-temperature Mössbauer measurements, which yields a closure temperature of 560 K and a cooling rate of 1.1 °C per  $10^3$  yr. Earlier room-temperature Mössbauer measurement of this sample by Ghose (1965) yielded 0.90 for  $X_{Fe}^{M2}$ , which yields a closure temperature of 460 K and a cooling rate of 2.1 °C/m.y. In this case, much of the discrepancy may be ascribed to the increased spectral resolution available at low temperatures. Mössbauer measurement of sample 274 by Virgo and Hafner (1970) yielded  $X_{Fe} = 0.172$ ,  $X_{Fe}^{M2} = 0.322$ ,  $T_c = 535$  K, and  $dT/dt = 219$  °C/m.y. Domeneghetti et al. (1985) measured the total Fe and ordering state of the same sample by single-crystal X-ray techniques and obtained  $X_{Fe} = 0.218$ ,  $X_{Fe}^{M2} = 0.420$ , which yields  $T_c = 485$  K and  $dT/dt = 0.124$  °C/m.y. These differences show that expected errors in total Fe and its partitioning may yield four orders of magnitude variation in calculated cooling rates. A detailed comparison of results on several samples measured in our laboratory with results on these same samples obtained elsewhere is being published separately (L. M. Anovitz, W. W. Zhao, W. R. Dunham, in prep.).

The method used to correct the measured composition for solid solutions also affects the result obtained. In this paper we have used the measured mole fraction of Fe (analyses normalized to two cations) rather than a value renormalized to Fe + Mg (Saxena and Ghose, 1971). Mössbauer spectroscopy measures the ratio of Fe in the two sites, rather than the absolute amount of Fe. Use of a value for total Fe greater than that actually present will bias the result toward more complete ordering. In addi-

tion, the presence of elements other than Fe and Mg in a natural sample should have an effect on ordering kinetics. Future corrections for other components should be made by improving the equilibrium (cf. Davidson and Lindsley, 1985, for Ca; Kawasaki and Matsui, 1983, for Al) and kinetic models for orthopyroxenes rather than by empirical projection schemes.

Despite these caveats, several predictions about the effects of various solid solutions may be made. Because Ca is concentrated in the M2 site, it should limit the Fe substitution in this site, thus raising the calculated equilibrium temperature and the calculated cooling rate. In contrast, Al ordering into the M1 and tetrahedral sites should lower the calculated equilibrium temperature and cause a decrease in the calculated cooling rate. Examination of the results for the natural samples with intermediate Fe values ( $0.3 \leq X_{\text{Fe}} \leq 0.5$ ) (Table 5) does not reveal correlations between cooling rate and Ca content. A possible correlation between Al content and cooling rate is observed that matches the predicted trend, but further experiments using samples with a range of Al contents will be necessary to evaluate this trend.

Two sources of errors exist in the equilibrium and kinetic models. These are errors due to the imprecision in the experimental measurements on which the models are based and the imprecision in the model obtained for the compositional dependence of the kinetic parameters. For M32b, the minimum and maximum ordering rates and equilibrium temperatures allowed by the standard errors in Equation 22 yield an error range of 0.5 to 100 °C/m.y. These errors are at present too large to allow the orthopyroxene geospeedometer to be used as more than an order-of-magnitude constraint on cooling rates in granulite terranes. As most of this error range is due to uncertainties in extrapolation of the equilibrium and kinetic models to temperatures well below the experimental data, the present model may yield much more useful data if applied to igneous or contact-metamorphic samples.

The standard errors for the compositional dependences of the kinetic model presented in Equations 30 and 31 reflect the imprecision in the fit to the average values for each composition. As the equilibrium model is based on the minimum number of constraints necessary to solve the equations, no standard-error estimate may be obtained. It must, however, be at least as large as those obtained for M32b and PX4-TM2 from which it was derived. The true error brackets for compositions other than those experimentally measured must reflect both this error and the error in the individual data points. The true error brackets are thus difficult to determine, but they should be at least as large as those for the measured data.

In conclusion, this study has shown that new ordering experiments for the equilibrium distribution of Fe between the M1 and M2 sites in orthopyroxene yield significantly lower closure temperatures than those suggested by previous studies. Lower equilibrium temperatures yield slower calculated cooling rates for these samples, bringing the calculated cooling rates for high-grade re-

gional metamorphic rocks into reasonable agreement with results obtained from other approaches.

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