

Reaction texture and Fe-Mg zoning in granulite garnet from Søstrene Island, Antarctica: Modeling and constraint on the time scale of metamorphism during the Pan-African collisional event

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Garnets from the Søstrene island, Antarctica, show reaction textures corresponding to two metamorphic episodes, one at c. 1000 Ma (M1) and the other at c. 500 Ma (M2). The latter is associated with a Pan-African tectono-metamorphic event that has been interpreted to represent a continent-continent collision followed by extensional collapse. Reaction-diffusion modeling of the compositional zoning of garnet associated with the development of reaction texture during M2 yields a time scale of ~ 5–16 Myr for the duration of the peak of this overprinting metamorphism at ~ 730 ± 20°C. The associated velocity of the reaction front is ~ 5.0–1.6 μm/Myr. The inferred duration of peak metamorphism during the Pan-African event seems to be in good agreement with the available U-Pb SHRIMP ages of zircon and monazite that may be interpreted to have formed at the beginning and end stages of crystallization of granite during the metamorphic peak.

1. Introduction

Søstrene Island, which is located in Prydz Bay, Antarctica (figure 1), belongs to an upper amphibolite to granulite facies metamorphic terrane that extends from the Munro Kerr Mountains in the west to the Rauer Group near Davis Station in the east. Thost *et al* (1991); Hensen and Zhou (1995a, b) and Hensen *et al* (1995) described two major episodes of granulite facies metamorphism, one at c. 1000 Ma (M1) considered to only affect the orthogneiss basement, and the other at c. 500 Ma (M2), affecting both basement and sedimentary cover rocks. These metamorphic ages were determined by the garnet Sm-Nd technique. Subsequent U-Pb age determinations of zircon in SHRIMP have essentially confirmed the widespread occurrence of the 500 Ma event in the metasedimentary rocks, which are considered to be a cover sequence of 1000 Ma old basement (Hensen *et al* 1995; Fitzsimons 1996; Car-

son *et al* 1996; Fitzsimons *et al* 1997). A comprehensive review of the tectonic history, integrated with the age data, can be found in Fitzsimons (2000).

Thost *et al* (1991) studied in detail the texture and reaction relations of garnets (figure 2; sample no. 8813007), which occur as large (2–3.5 cm) lenticular to irregular shaped grains. They found the garnets to be mantled by a 0.5–1.5 cm wide corona of plagioclase + orthopyroxene symplectite and minor hornblende, magnetite and ilmenite. This corona separates garnet from the matrix, which is composed of clinopyroxene and hornblende ± orthopyroxene ± plagioclase. The garnets show closely spaced thin (0.5–0.6 mm) subparallel fractures, within which there is a different set of fine grained symplectites consisting of orthopyroxene, plagioclase and spinel.

According to Hensen *et al* (1995), the outer coarse-grained coronas around the garnets developed during the course of decompression following

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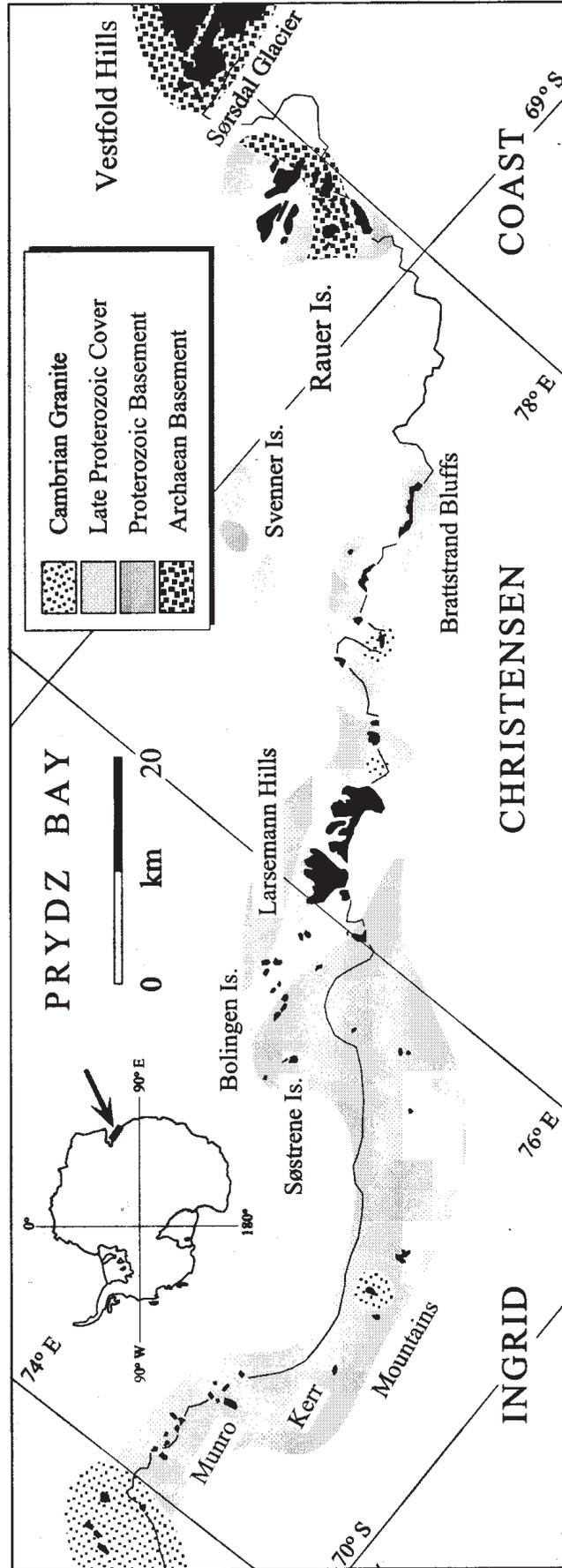


Figure 1. Geologic map of the Prydz Bay coastline, eastern Antarctica, showing the distribution of proterozoic felsic and mafic lithologies (presumed basement) and the pelitic rocks (presumed cover), after Hensen *et al* 1995).

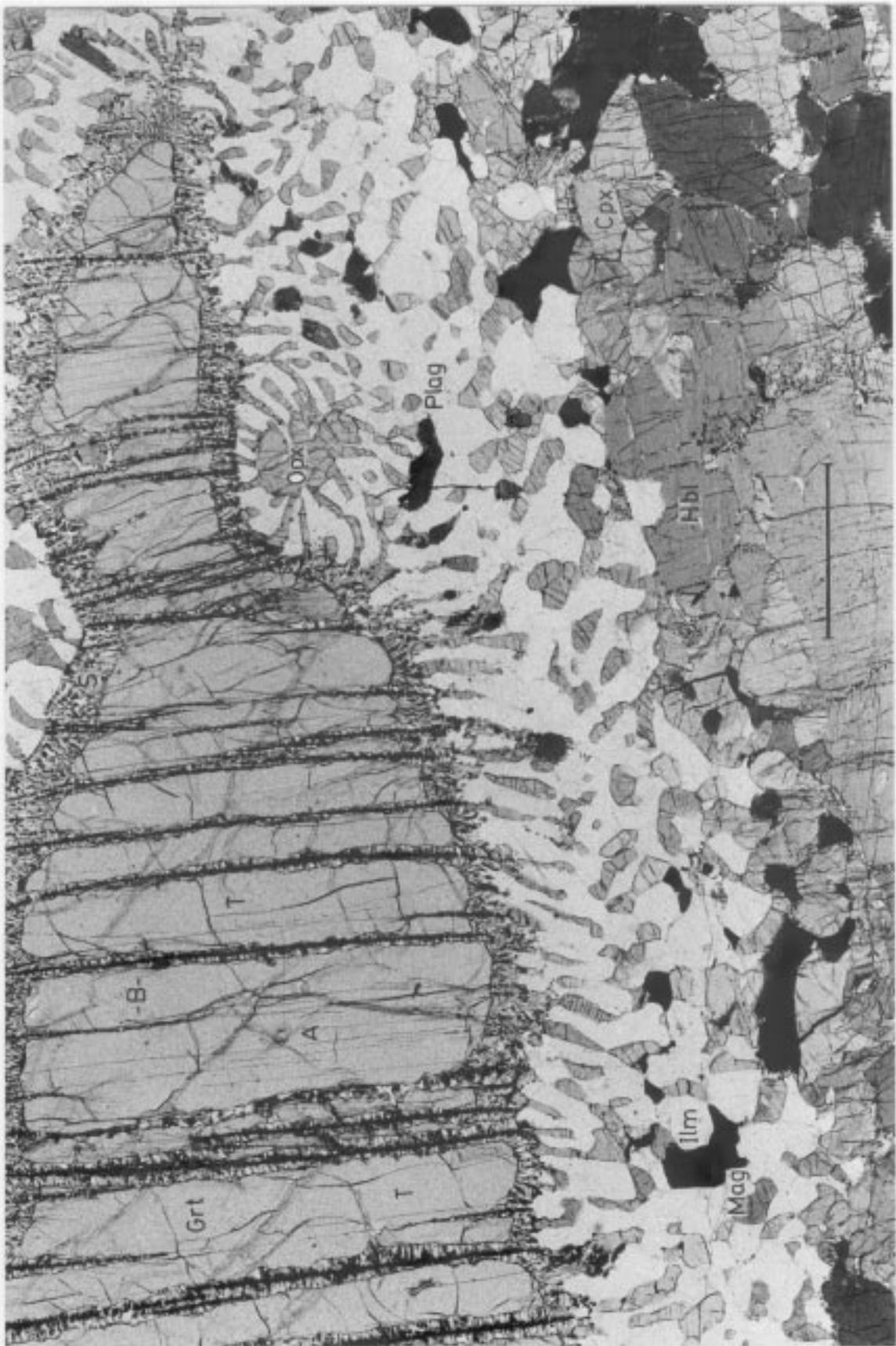


Figure 2. Photomicrograph showing the reaction texture and fracture cleavage of a large garnet grain in the sample 881307. The coarse grained outer symplectite, interpreted to have developed during the M1 decompression, consists of orthopyroxene (Opx) and plagioclase (Pl), with minor hornblende (Hbl) and magnetite (Mag)-ilmenite (Ilm) intergrowths. The finer grained inner (M2) symplectite mantling the grain and within the fracture zones consist of Opx, Plag and spinel (Spl) (+Mag-Ilm). Scale bar is 1.7 mm.

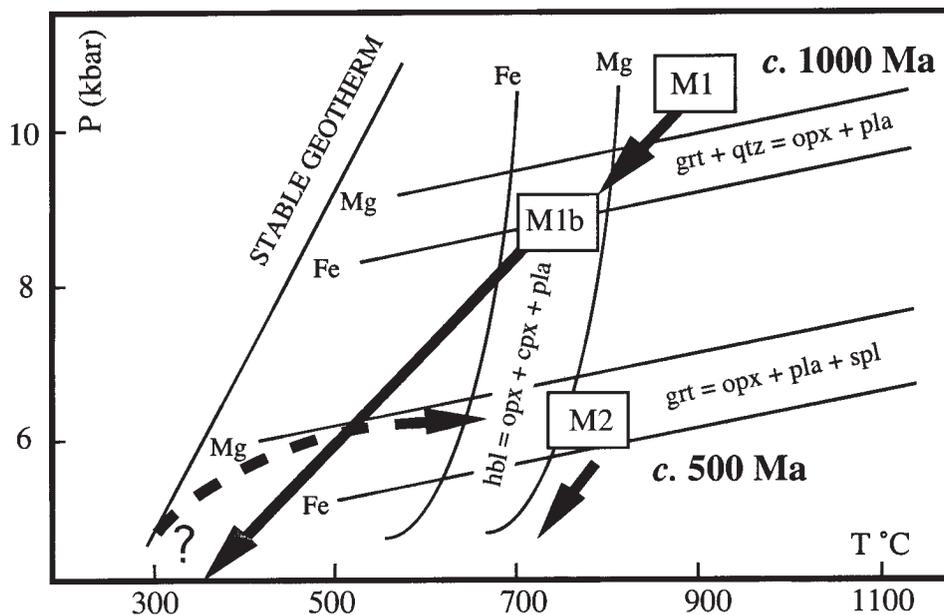


Figure 3. Two stage P-T history (M1-M1b followed by M2) of Søstrene island granulites, as deduced by Hensen *et al* (1995) from geochronological and thermo-barometric constraints. Lines labeled Fe and Mg show the limits of garnet and hornblende breakdown reactions for Fe and Mg end member compositions, respectively. Reproduced from Hensen *et al* (1995).

the M1 metamorphism at the peak condition of ~ 10 kbar, $850\text{--}900^\circ\text{C}$, which resulted in the retrograde breakdown of garnet according to $\text{Grt} + \text{Qtz} \rightarrow \text{Opx} + \text{Plag}$. The fracture-cleavage in garnets and the included fine-grained symplectites are believed to have developed during a regional Pan-African event at 500 Ma. This event was accompanied by intense deformation over most of the Prydz Bay region, and has been interpreted to represent a collisional event followed by extensional collapse (Fitzsimons 1996, 2000). Figure 3, which is reproduced from Hensen *et al* (1995), illustrates the interpretation, by these authors, of the polymetamorphic history of the granulites in Søstrene Island. The fine-grained symplectites, which represent the breakdown products of garnet according to $\text{Grt} \rightarrow \text{Opx} + \text{Plg} + \text{Spl}$, are believed to have formed at the peak of the M2 metamorphism, possibly during early isothermal decompression.

Compositional zoning in garnet occurs between the closely spaced fractures, and must have developed by a process of reaction-diffusion during the M2 metamorphism (Thost *et al* 1991; Hensen *et al* 1995). The purpose of this paper is to carefully study the compositional zoning in order to constrain the duration of metamorphism over which the zoning developed. As a by-product, the same analysis also yields the rate of advancement of the symplectite into the garnet during this metamorphism.

2. Compositional zoning in garnet

2.1 Measurement and modeling framework

We determined the compositional zonings in garnet normal to the trace of fractures in the thin section by beam scanning in an electron microprobe. Ideally, the compositional zoning should be measured normal to the plane of the fracture cleavage. Deviation of this plane from normalcy to the plane of thin section would cause a geometric enlargement of the measured diffusion profile relative to its true length (normal to the fracture plane), and, consequently, an overestimation of the time scale. In this study, we have not been able to determine the orientation of the plane of fracture cleavage. However, as shown by Ganguly *et al* (2000), the overestimation of time is negligible as long as the fracture plane or interface is not rotated by more than 30° from the vertical.

A representative zoning profile of garnet is shown in figure 4. The step size for the measurement of compositional zoning was variable, with a small step size, $\sim 1.4\ \mu\text{m}$, within the diffusion zone, and a coarser step size, $\sim 5\ \mu\text{m}$, in the homogeneous segment. This strategy was adopted to compromise between the need for high spatial resolution within the diffusion zone and the total time spent on measuring a zoning profile. No significant difference was found among the zoning profiles that were measured along different traverses, irrespective of the nature of the contacting phase, whether it is

orthopyroxene or spinel or plagioclase. The symplectite minerals were found to be compositionally homogeneous, and showed very little grain to grain compositional variation. This is presumably due to relatively rapid grain boundary diffusion through the fine-grained symplectite matrix.

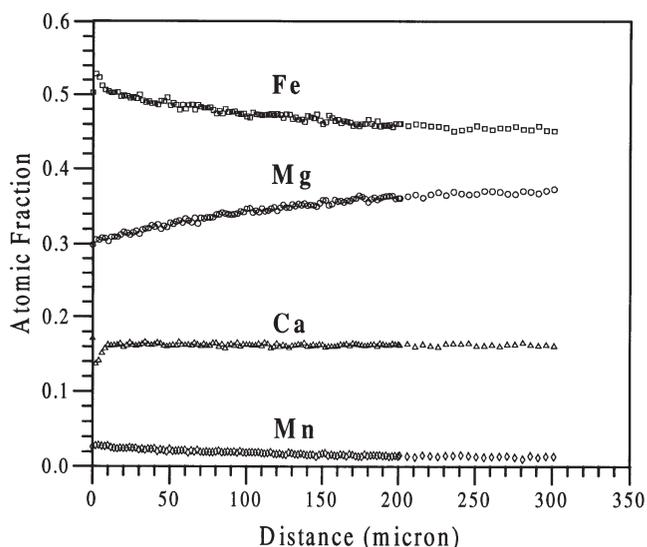


Figure 4. Compositional zoning of divalent cations in garnet in the sample 881307, as measured by beam scanning in an electron microprobe normal to the trace of a fracture cleavage that developed during M2.

Full microprobe analyses were carried out at each spot using 15 kV accelerating voltage, 15 nA beam current, and counting for 20 s. The standards were as follows: synthetic pyrope, grossular, spessartine and diopside for Mg, Ca, Mn and Si respectively; natural olivine, jadeite, sphene, chromite, feldspar for Fe, Na, Ti, Cr, K, respectively, and Ni-diopside glass for Ni. All iron was treated as Fe^{2+} . In any acceptable analysis, the positive charge deficiency is within 0.5%, which implies very small amounts of Fe^{3+} in garnet and orthopyroxene.

It is evident from the textural relation discussed above that the zoning profile in garnet normal to the fracture cleavage developed simultaneously with its breakdown to $\text{Opx} + \text{Spl} + \text{Pl}$ during the M2 metamorphism (Hensen *et al* 1995). Consequently, the modeling of the zoning profile must incorporate the effect of movement of the boundary between the garnet and its reaction products within the fracture cleavages. We assume that the reaction-diffusion process took place at an isothermal condition, which is reflected by the Fe/Mg distribution coefficient between the symplectite orthopyroxene and garnet rim. We refer to this distribution coefficient as rim- K_D or $K_D(\text{Grt}_{\text{rim}}\text{-Opx})$, where $K_D = (\text{Fe}/\text{Mg})^{\text{Grt}} / (\text{Fe}/\text{Mg})^{\text{Opx}}$.

The assumption of isothermal condition implies a fixed edge composition of garnet during diffu-

sion, provided that there was no 'leakage' of components from the interface. It is possible that the reaction-diffusion took place over a range of temperature, in which case the temperature reflected by this rim-KD defines the lowest temperature at which this process was effective. However, it has been our experience (e.g. Liermann and Ganguly 2001) that compositional zoning that developed during cooling and thus involved a continuous change of the rim composition can not be fitted well by compositional profiles calculated for an isothermal condition. Therefore, the goodness of fit (see below) probably provides a test or the validity of the assumption of isothermal versus non-isothermal process.

In the data illustrated in figure 4, the diffusion profiles of Fe and Mg show essentially complementary compositional changes over a distance of $\sim 250 \mu\text{m}$ from the margin. The Ca and Mn profiles are almost flat except that there is a sudden drop of Ca content (accompanied by a complementary rise of Fe content) within the first $10 \mu\text{m}$ from the interface. This drop of Ca was probably due to the M2 symplectite reaction $\text{Grt} = \text{Opx} + \text{Pag} + \text{Spl}$. Because the change of Ca content of garnet is limited only to a 10 mm thin rim, we treated the diffusion process associated with the development of compositional zoning of Fe and Mg as a binary diffusion of these components. Figure 5 shows the normalized diffusion profile of Mg such that at any point, $\text{Mg}/(\text{Mg} + \text{Fe}) + \text{Fe}/(\text{Mg} + \text{Fe}) = 1$. As we would see later, the data within the first 10 mm from the interface have no significant effect on the final results of modeling of the compositional zoning.

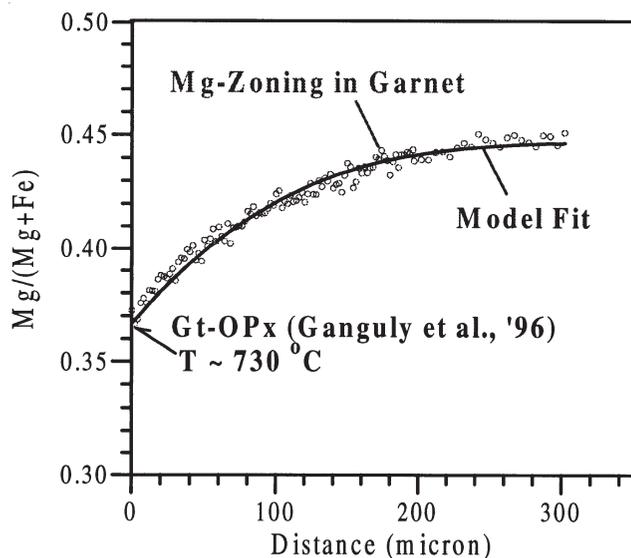


Figure 5. Normalized $\text{Mg}/(\text{Mg} + \text{Fe})$ concentration profile in garnet as derived from the data illustrated in figure 4, and the model fit (solid line) using an isothermal reaction-diffusion model.

2.2 Thermometry and calculation of $D(\text{Fe-Mg})$

The temperature for the assumed isothermal reaction-diffusion process is calculated from the $K_D(\text{Grt}_{\text{rim}}\text{-Opx})$ and the thermometric formulation of equilibrium Fe-Mg fractionation between garnet and orthopyroxene of Ganguly *et al* (1996). The latter is based on the optimized garnet solution model (Ganguly *et al* 1996) and the (reversed) experimental data of Lee and Ganguly (1988) on the equilibrium fractionation of Fe and Mg between garnet and orthopyroxene, using crystalline mixtures. Representative rim compositions of garnet and orthopyroxene are summarized in table 1. The compositions were measured at spots at $\sim 3\text{--}5\ \mu\text{m}$ from the interface. Combinations of garnet rim and adjacent orthopyroxene compositions yield $T \sim 730 \pm 20^\circ\text{C}$ at $P = 6\text{ kb}$, which is in good agreement with that inferred by Thost *et al* (1991) and Hensen *et al* (1995) as the peak temperature of M2 metamorphism at the same pressure (figure 3). The agreement between the temperature obtained from the rim- K_D and the independently estimated peak temperature also suggests that the compositional zoning of garnet developed and froze before the rock experienced sufficient cooling following peak M2.

Table 1. Selected compositions of garnet and orthopyroxene in the granulite sample No. 8813007 from the Sostrene Island. The rim compositions are at 3–5 microns from the interface.

Wt%	Grt		Opx	
	Rim	Core	Rim	Center
FeO	25.61	22.05	20.57	20.99
MgO	7.89	10.15	23.24	22.75
CaO	4.56	6.03	0.23	0.22
MnO	1.39	0.75	0.36	0.40
Al ₂ O ₃	21.71	22.13	3.25	3.82
SiO ₂	37.96	38.90	50.99	50.44
Total cations	99.12	100.02	98.64	98.62
Fe	1.67	1.40	0.32	0.33
Mg	0.92	1.15	0.65	0.63
Ca	0.38	0.49	0.00	0.00
Mn	0.09	0.05	0.01	0.01
Al	1.99	1.97	0.07	0.08
Si	2.95	2.95	0.95	0.94

The cation proportions in garnet and orthopyroxene are on 12 and 3 oxygen basis, respectively.

The self-diffusion coefficients (D^*) of Fe and Mg at this temperature were calculated from the data of Ganguly *et al* (1998). These D^* data were then

used to calculate $D(\text{Fe-Mg})$ according to (Manning 1968)

$$D(\text{Fe-Mg}) = \frac{D^*(\text{Fe})D^*(\text{Mg})}{X_{\text{Fe}}D^*(\text{Fe}) + X_{\text{Mg}}D^*(\text{Mg})} \quad (1)$$

where $X_{\text{Fe}} = \text{Fe}/(\text{Fe} + \text{Mg})$ and $X_{\text{Mg}} = 1 - X_{\text{Fe}}$. There are two sets of D^* data in Ganguly *et al* (1998), one derived from experiments in pyrope-almandine diffusion couple, and the other from those in spessartine-almandine diffusion couple, as determined by Chakraborty and Ganguly (1992). At the P-T condition of interest, $D^*(\text{Mg})$ is nearly the same, but $D^*(\text{Fe})$ is significantly different, in the two types of diffusion couple experiments. We have used the D^* data for pyrope-almandine diffusion couple since its composition is similar to that of the sample.

To take advantage of the analytical solution of the diffusion equation, which assumes a constant D (see below), we calculated $D(\text{Fe-Mg})$ at the middle of the diffusion zone ($X_{\text{Mg}} = 0.41$), and used this value to model the diffusion process. Thus, we have $D = 1.39 \times 10^{-19}\text{ cm}^2/\text{s}$ and $5.21 \times 10^{-19}\text{ cm}^2/\text{s}$ at the limiting temperatures of 710 and 750°C that were calculated above for the equilibration of garnet rim and orthopyroxene grains within the symplectite matrix. The $D(\text{Fe-Mg})$ value calculated at any point within the diffusion zone is within 10% of its value at $X_{\text{Mg}} = 0.41$. Thus, it is easy to see that the error introduced by the assumption of compositional independence of D , and fixing it to the value at the middle of the diffusion zone, is much smaller than that arising from the uncertainty in the temperature estimate.

2.3 Modeling of the zoning profile

With the above framework, the diffusion problem may be mathematically formulated as follows, assuming that the core composition of the garnet was not affected by diffusion (see below for justification), and that the diffusion coefficient had remained constant. The garnet-matrix interface is set at $x = 0$, and is assumed to have moved with a constant velocity v towards a fixed marker point at $x > 0$. Then the diffusion equation to be solved is

$$\frac{dC}{dt} = D \frac{d^2C}{dX^2} + v \frac{dC}{dx} \quad (2)$$

with the initial and boundary conditions

$$\begin{aligned} C &= C_o & \text{at } x > 0, t = 0 \\ C &= C_r & \text{at } x = 0, t > 0. \end{aligned}$$

The solution to this diffusion equation can be easily obtained as a special case of that obtained by

Carslaw and Jaeger (1959, p. 388, equation 7) for heat conduction in a moving body. The solution is

$$C(x) = C_o + \frac{1}{2}(C_r - C_o) \left[\operatorname{erfc} \left(\frac{x + vt}{2\sqrt{D_t}} \right) + \exp \left(\frac{-vx}{D} \right) \operatorname{erfc} \left(\frac{x - vt}{2\sqrt{D_t}} \right) \right]. \quad (3)$$

The above equation was used earlier by Loomis (1975) for treating the reaction-diffusion problem in garnet from the metamorphic aureole around the Ronda ultramafic intrusion in southern Spain.

We assume that the breakdown of garnet within a fracture cleavage (according to $\text{Grt} \rightarrow \text{Opx} + \text{Pl} + \text{Spl}$) proceeded symmetrically in both directions normal to the fracture. Thus, the half-width of the symplectite zone within the fracture-cleavage that terminates the measured diffusion profile is taken to represent the thickness of the reaction zone (R_z) that developed during the reaction-diffusion process in one direction. This yields $R_z \sim 25 \mu\text{m}$. We also have $v = R_z/t$, which can be substituted in equation (3) to reduce the number of variables by one. $C(x)$ can then be solved in terms of time (t) from the above value of $D(\text{Fe-Mg})$ and the measured diffusion profile.

Modeling of the measured compositional zoning in garnet according to equation (3) was carried out by linking it with a well known non-linear optimization program, MINUIT (James and Roos 1975). The initial composition, C_o and the time, t , were the floating variables. The optimization program works through preliminary fitting of the data by Monte Carlo search of the optimum values of the floating parameters, followed by refinements according to the Simplex (Nelder and Mead 1965) and Migrad (Fletcher 1970) methods. This procedure yields a value of C_o which is essentially the same as the measured core composition of garnet, and $t = 5\text{--}16 \text{ Myr}$ for the duration peak M2 metamorphism at the inferred temperature of $750\text{--}710^\circ \text{C}$. At the mean value of the estimated peak temperature of 730°C , $t \sim 8 \text{ Myr}$. The calculated profile is compared with the measured zoning data in figure 5. Neglecting the first three data points (which cover the distance over which Ca content of garnet shows a sudden drop e.g. figure 4), have very little effect on the modeling. The retrieved value of t and the observed half-width of the symplectites within the fracture-cleavage yields v (i.e. the resorption rate of garnet normal to the fracture-cleavage during M2) as $\sim 5.0\text{--}1.6 \mu\text{m/Myr}$. This resorption rate is around a factor of 250 to 1000 slower than the inferred growth rate of garnet in low to medium grade regional metamorphic

rocks (Christensen *et al* 1989; Vance and O'Nions 1990).

3. Time-scale peak metamorphism during the Pan-African event

If the compositional zoning in garnet had developed during cooling, then the time scale for the reaction-diffusion process would be shorter than that inferred above (5–16 Myr) for the case of an isothermal process at 725°C . It is also possible that the compositional zoning developed during a combined heating and cooling regime. However, because of the very good match between the measured and calculated compositional profile according to isothermal model, we believe, for reasons discussed above, that the reaction-diffusion process took place at nearly isothermal condition.

There are potential uncertainties in the retrieved value of the time scale arising from those of the calibration of Grt-Opx geothermometer and the diffusion data. However, cooling rates estimated from the chosen diffusion data and compositional zoning in garnet have been found to be in good agreement with those constrained by geochronological data and the closure temperatures of the decay systems (Spear and Parrish 1996; Weyer *et al* 1999). Also the thermometric formulation has been well tested (Ganguly *et al* 1996). On the other hand, both the deviation of the interface from normalcy to the plane of thin section and consideration of reaction-diffusion during cooling or decompression would reduce the time estimate for the peak metamorphism. Thus, the estimated upper limit of $\sim 16 \text{ Myr}$ for the peak metamorphism during the 500 Ma Pan-African event is unlikely to be in serious error.

Fitzsimons *et al* (1997) have reported SHRIMP U-Pb ages of zircon and monazite in leucogneiss from Prydz Bay. They suggested that the older $535 \pm 13 \text{ Ma}$ zircon age represents the initial stages of leucogranite crystallization, whereas the younger $518 \pm 3 \text{ Myr}$ monazite age constrain the timing of final melt crystallization. Here the uncertainties represent $\pm 2\sigma$ values. Fitzsimons (pers. comm.) suggested that the difference between the zircon and monazite ages, which is $17 \pm 13 \text{ Myr}$, constrains the duration of the peak Pan-African metamorphism in the Prydz Bay area, when the temperature was high enough to produce granite melt. It is interesting to note that the duration of peak M2 calculated from modeling compositional zoning of garnet is included within the time scale that seems to be constrained by geochronology. We, thus, conclude that the duration of peak metamorphism during the Pan-African event was probably not significantly in excess of 16 Myr.

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