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# Modeling of retrograde diffusion zoning in garnet: evidence for slow cooling of granulites from the Highland Complex of Sri Lanka

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#### Summary

Diffusion modeling of zoning profiles in garnet rims from mafic granulites is used to estimate cooling rates in the Proterozoic basement of Sri Lanka, which represents a small, but important fragment of the Gondwana super-continent. Metamorphic peak temperatures and pressures, estimated with two-pyroxene thermometry and garnet–clinopyroxene–plagioclase–quartz (GADS) barometry, yield  $875 \pm 20$  °C and  $9.0 \pm 0.1$  kbar. These peak metamorphic conditions are slightly higher than results obtained by garnet-biotite Fe–Mg exchange thermometry of  $820 \pm 20$  °C. Reset flat zoning profiles were observed in most garnets. Only narrow garnet rims touching biotite exhibit retrograde zoning in terms of Fe and Mg exchange.

The garnet zoning observed requires a slow cooling history. Equilibrium was achieved along grain boundaries during or close to peak metamorphism. During subsequent cooling to lower temperatures, only local exchange between garnet and biotite occurred. A cooling rate of 1-5 °C/Ma is estimated. The estimated temperature-time history from garnet profiles is in good agreement with the cooling history inferred from mineral radiogenic ages in the literature.

# Introduction

Cooling rates of rocks are usually determined in three different ways: using closure temperature of minerals for radiogenic isotopes (e.g. *Dodson*, 1973; *Mezger* et al., 1992); or for stable isotopes (e.g. *Eiler* et al., 1992, 1995); or diffusive zoning in

metamorphic minerals (e.g. Lasaga, 1983; Florence and Spear, 1995). To quantify the cooling history of rocks, many workers have discussed the use of garnet diffusive zoning patterns. Some have used the assumption of a large amount of (infinite) biotite, which implies a fixed biotite composition that is unaffected by diffusional exchange with the garnet (e.g., Dodson, 1973; Ehlers et al., 1994). This assumption is correct for some granulites, where biotite makes up more than 30% of the rock volume and diffusion along grain boundaries is fast (e.g., Dodson, 1973). If there is not enough biotite in the rock, the diffusional fluxes of the elements between biotite and garnet grains directly in contact must be balanced (e.g., *Ehlers* and *Powell*, 1994; Florence and Spear, 1995). The diffusional gain or loss in garnet is balanced by the compositional change of its coexisting biotite. Fe-Mg inter-diffusion between more than two minerals, such as between garnet, biotite and clinopyroxene, requires that all fluxes between these minerals are balanced in a closed system. Hence, the knowledge of interdiffusion coefficients of all individual phases and the modal abundances of these phases are required (see Eiler et al., 1992 for more details).



Fig. 1. Simplified geological map of Sri Lanka and the geology in the area around Rupaha (after *Cooray*, 1994 and *Kröner* et al., 1991). The inset shows the four basement units in Sri Lanka: *HC* Highland Complex; *VC* Vijayan Complex; *WC* Wanni Complex. The unlabeled small unit in the center of the inset is the Kadugannawa Complex

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Lower crustal granulites are commonly exposed in Gondwana fragments, such as the small fragment of Sri Lanka. Granulites in Sri Lanka often contain significant amounts of mafic rocks, which are interpreted as metamorphosed basic igneous rocks. These granulites often show consistent isobaric cooling in the area around Rupaha within the Highland Complex (Fig. 1). Here we use these granulites to evaluate the thermal evolution of this region. Up to now only a few studies have presented cooling rates for Sri Lankan granulites (*Burton* and *O'Nions*, 1990; *Hölzl* et al., 1991) and we compare our results to these previous studies.

We use diffusive zoning profiles in garnet to determine cooling rates of the basement complex. Our interpretations are based on: (1) recovering the composition of garnets at peak metamorphic conditions and (2) application of diffusion models to estimate the cooling rates by matching numerically calculated zoning patterns with observed ones. The results are combined with geochronology from the literature to describe the complete exhumation history of the granulites.

# **Geological setting**

The Proterozoic basement of Sri Lanka exposes substantial parts of lower continental crust in which four different units were distinguished on the basis of isotopic, geochronological, geochemical and petrological constraints (Cooray, 1994; Kröner et al., 1991; Milisenda et al., 1994) (Fig. 1): (1) the Highland Complex (HC); (2) the Vijavan Complex (VC); (3) the Wanni Complex (WC) and (4) the Kadugannawa Complex (KC). The Wanni Complex consists mainly of metabasites and charnockites whereas the Highland Complex is comprised of interbedded metapelites, quartzites and marbles in addition to garnet-biotite gneisses and charnockites. The Vijayan Complex is exposed in eastern Sri Lanka, consisting of meta-igneous gneisses of tonalitic to leucogranitic composition. The Highland Complex rocks yield relatively old crustal residence Sm–Nd model ages of 2–3 Ga (*Milisenda* et al., 1994), while rocks from the other units give significantly younger ages of 1-2 Ga. Metamorphic grade reaches granulite facies throughout the Highland, the Wanni and the Kadugannawa Complexes, but rocks are locally retrogressed to amphibolite facies. In contrast, the Vijayan Complex is characterized by amphibolite facies assemblages. The timing of peak metamorphism was estimated between ~550-610 Ma (Hölzl et al., 1991; Kröner et al., 1991).

The area of this study is located in the central part of Sri Lanka, within the central granulite belt of the Highland Complex at Rupaha (Fig. 1). It consists mainly of meta-igneous rocks (orthogneisses and charnockitic gneisses), which are intercalated with metasediments (quartzites, garnet-sillimanite-graphite gneisses, garnet-biotite gneisses, corundum-biotite gneisses and minor calc-silicates, marbles and ultramafics). The small-scale structures and geological units in the study area are illustrated in Fig. 1.

# Petrography

Two rock types of mafic granulites, differing in mineral paragenesis and modal proportions, were used for geothermobarometric calculations and geospeedometry:

1) garnet–biotite gneisses (sample location No. 9708 in Fig. 1) and 2) charnockites (sample location No. 9817 in Fig. 1).

Garnet-biotite-bearing gneisses are coarse-grained and dark rocks with a strong schistosity. Mineral assemblages are typically  $Grt + Bt + Pl + Qtz \pm Ilm$ ;  $Grt + Bt + Cpx + Pl \pm Qtz \pm Ilm$ ;  $Grt + Cpx + Pl \pm Qtz \pm Ilm$  (abbreviations after *Kretz*, 1983). Garnet contains inclusions of plagioclase and biotite. Some parts of the rocks are migmatized. In garnet-biotite-bearing gneisses, no reaction textures are observed (Fig. 2a). Garnet-quartz grain boundaries are absent suggesting that the reaction garnet + quartz to clinopyroxene + plagioclase has occurred. Biotite and garnet are in textural equilibrium in many places (Fig. 2a).

Charnockites are characterized by the mineral paragenesis  $Opx + Kfs + Pl + Qtz \pm Ilm \pm Ap$ ;  $Hbl + Opx + Pl + Kfs + Qtz \pm Ilm \pm Ap$ ;  $Opx + Cpx + Hbl + Pl + Qtz \pm Ilm \pm Ap \pm Grt$ . The quartz content varies in these rocks from a few up to about 10 vol.%. Both pyroxenes in charnockites are generally devoid of



Fig. 2. Backscattered electron images of co-existing garnet–biotite, garnet–clinopyroxene, garnet–plagioclase and garnet–garnet in a garnet biotite gneiss (sample 9708) at Rupaha, Sri Lanka. Chemical composition profiles were run across garnets along lines A–B, C–D, E–F, G–H, J–K, L–M

inclusions, though some small rounded grains of hornblende and plagioclase may be present. Large elongated crystals of hornblende in the matrix have irregularshaped edges. A few grains of biotite are present in some samples of the two-pyroxene-hornblende-bearing assemblages. Some late stage chlorite replaces hornblende. The primary metamorphic mineral assemblages selected for thermobarometric studies are Opx-Cpx-Pl-Hbl-Qtz and Grt-Bt-Cpx-Pl-Qtz along with minor amounts of magnetite, ilmenite, apatite, rutile and zircon.

#### Analytical techniques

Samples from both rock types showing the primary mineral assemblages with no or minor retrogression were selected for thermobarometry. After detailed optical inspection of polished thin sections, mineral analyses were performed on carbon-coated thin sections at the University of Mainz, Germany, using the JEOL microprobe (JEOL JXA 8900 RL) with operating conditions of 15 kV accelerating voltage, 12 nA beam current and 2 µm beam diameter. Elements were calibrated against synthetic and natural standards. Online ZAF corrections were performed (Amstrong, 1988). Mineral compositions of coexisting garnet-biotite, garnetclinopyroxene, and garnet-clinopyroxene-plagioclase-quartz from garnet-biotite gneisses and coexisting two-pyroxenes from the charnockites were analyzed. Garnets in textural equilibrium with either biotite or clinopyroxene were analyzed for both rim and core compositions. Some representative garnets, adjacent to biotite were investigated for zoning patterns by running microprobe line profiles across the grains, at a 3 µm spacing, and measuring for Fe, Mg, Ca and Mn. All iron was assumed to be  $Fe^{2+}$  on recalculation. For a later interpretation of the sectioning effect of garnet crystals, line profiles were measured across a range of apparent grain sizes in thin section between  $250 \,\mu\text{m}$  and  $700 \,\mu\text{m}$  in diameter.

#### **Mineral chemistry**

Selected mineral analyses from both the garnet-biotite gneisses and the charnockites are shown in Table 1. The comprehensive analytical data set can be obtained from the first author upon request.

Garnets in both rock types are mainly almandine–pyrope–grossular solid solutions, with average almandine contents around 50%. The pyrope content is around 21% whereas grossular and spessartine content are 16% and 13% respectively. Grains are typically about 500–600  $\mu$ m in diameter. The largest are about 700–800  $\mu$ m, the smallest about 100–200  $\mu$ m. Figure 2 shows back-scattered images of garnets with surrounding matrix and Fig. 3 the corresponding microprobe line profiles. Flat zoning of garnet is observed throughout most grains except in the vicinity of adjacent biotite, where X<sub>Mg</sub> decreases and X<sub>Fe</sub> increases slightly towards the garnet rim. These rims are approximately 40  $\mu$ m wide (Fig. 3). Garnet is typically unzoned towards non-Fe–Mg minerals (e.g., plagioclase) or other garnet (e.g., profiles E–F, J–K and L–M on Figs. 2,3). Garnet is not zoned with respect to Ca. The modal abundance of biotite is approximately half of the modal abundance of garnet. Biotite inclusions are preserved in some garnet grains. No zoning was found in clinopyroxene. Fe/(Fe + Mg) in clinopyroxene varies from 0.28–0.30 in

58	l I	I	40	G. 0 9	W.	A. F	R. F τ σ	ern ∾	anc	lo N	et a	al.	1	5	6	1		5	Э	4	
		Cpx core 6	52.0 0.2	0.0	10.2	1.2	21.0	0.5	pu	0.0	pu	pu	100.5	1.9	0.0	0.0	0	0.3	0.7	0.0	0
	-Pl-Qtz ges	Pl matrix 8	61.45 0.00	23.80 0.05	0.05	0.00	5.57	8.40	0.00	0.48	nd	pu	99.83	2.74	1.25	0	0	0	0	0	0
	Grt–Cpx assembla 9708A	Grt core 12	38.52 0.04	$21.32 \\ 0.05$	23.50	6.27 5 50	5.99	0.01	nd	nd	0.00	0.02	101.30	2.98	1.94	0	0	1.52	0.64	0.41	0
	x iges	Cpx core 6	50.65 0.09	$1.22 \\ 0.05$	18.44	0.38 8 15	0.4 <i>.</i> 0 20.75	0.51	nd	nd	nd	nd	100.55	1.96	0.06	0	0	0.60	0.49	0.01	0
culations at Rupaha	Opx–Cp assembla 9817	Opx core 6	48.33 0.08	0.68 0.05	38.03	0.89	0.87	0.01	pu	nd	pu	nd	99.61	1.97	0.03	0	0	1.29	0.65	0.03	0
	Grt-Cpx assemblages 9708	Cpx rim 6	52.19 0.11	$1.57 \\ 0.00$	9.52	1.00	21.39	0.34	0.00	0.02	0.00	0.00	99.68	1.96	0.07	0.00	0.00	0.30	0.76	0.03	0.00
ometry calc		Grt rim 12	38.65 0.08	21.15 0.10	23.30	6.25 5 11	6.05	0.19	0.00	0.00	0.13	0.08	101.43	2.99	1.93	0	0.01	1.51	0.63	0.41	0
ieral assemblages used for thermobar	Grt-Bt assemblages 9708	Bt matrix 11	38.07 5.26	12.89 0.00	14.35	0.14	0.16	0.22	0.24	8.65	1.55	0.35	95.43	2.73	1.09	0.28	0	0.86	1.45	0.01	0.01
		Bt at Grt contact 11	37.18 5.67	13.18 0.10	14.63	0.05	0.21	0.21	0.31	9.08	1.63	0.31	99.66	2.66	1.11	0.31	0.01	0.88	1.51	0.01	0.01
		Grt core 12	37.95 0.08	21.21 0.06	22.98	5.81 5.66	5.96	0.11	pu	pu	0.09	0.03	99.94	2.97	1.96	0.01	0	1.50	0.66	0.39	0
ions of min		Grt rim 12	38.24 0.06	21.43 0.05	23.61	5.91 5.48	5.92	0.07	nd	nd	0.00	0.01	100.78	2.97	1.96	0.00	0	1.53	0.64	0.39	0
Table 1. Composit	Assemblage sample no. mineral	No. of oxygens	SiO <sub>2</sub> TiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub> Cr <sub>2</sub> O <sub>3</sub>	FeO	MnO		$Na_2O$	BaO	$K_2O$	F	CI	Total	Si	Al	Ti	Cr	Fe	Mg	Mn	Ba

(continued)

Table 1 (continued	(l)										
Assemblage sample no. mineral	Grt–Bt assemb 9708	lages			Grt–Cp assemb 9708	x lages	Opx–C assembi 9817	px lages	Grt–Cp assemb] 9708A	x–Pl–Qtz lages	
No. of oxygens	Grt 12 12	Grt core 12	Bt at Grt contact 11	Bt matrix 11	Grt 12 rim	Cpx rim 6	Opx core 6	Cpx core 6	Grt core 12	Pl matrix 8	Cpx core 6
Ca Na K Total Cations	0.49 0.01 <b>8</b>	0.50 0.02 <b>8</b>	0 0.03 0.83 <b>7.36</b>	0.01 0.03 0.79 <b>7.25</b>	0.50 0.03 <b>8</b>	0.86 0.03 0.00 <b>4</b>	0.04 0 <b>0.4.02</b>	0.86 0.04 0 <b>4.02</b>	0.50 0 8	0.27 0.73 0.03 <b>5.01</b>	0.85 0.04 0 <b>4.02</b>
F CI	0 0	0.02 0	0.37 0.04	$0.35 \\ 0.04$	0.03 0.01	0 0	0 0	0 0	0 0	0 0	0 0
X almandine X pyrope X grossular	0.50 0.21 0.16 0.13	0.49 0.22 0.16 0.13			0.49 0.21 0.16 0.13				0.49 0.21 0.16 0.13		
Fe/(Fe + Mg)			0.37	0.37		0.28	0.67	0.55			0.30
FeO as total fe: no	I not detec	table									

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biotite gneisses and between 0.51-0.55 in charnockitic rocks. Orthopyroxene in charnockites is of homogeneous composition and has a Fe/(Fe + Mg) value of 0.64-0.67.

#### Pressure-temperature estimates and water activity of fluid phase

Results of ion exchange thermometry (Table 2) are based on the garnet-biotite (Dasgupta et al., 1991), the garnet-clinopyroxene (Sengupta et al., 1989) and the orthopyroxene-clinopyroxene (Brey and Köhler, 1990) equilibria. Pressures were determined by using the garnet-clinopyroxene-plagioclase-quartz (GADS) barometer (*Eckert* et al., 1991). Temperature and pressure were calculated by simultaneously solving the barometric and temperature equations, where applicable (Fig. 4). The highest P-T estimates were obtained for Opx-Cpx thermometry together with GADS barometer. Temperatures range from 865-890 °C, with pressures of 8.9-9.1 kbar. All three calibrations (Lindsley et al., 1981; Kretz, 1982; Brey and Köhler, 1990) yield identical results within the variation of mineral chemistry. Temperatures of 775-840 °C were obtained from Grt-Bt/GADS, using garnet cores, at pressures of 7.6–8.3 kbar. These are lower than the Opx–Cpx/GADS thermobarometer values presented above. Pressure-temperature estimates obtained from garnet rims and adjacent biotite compositions with the GADS barometer range from 685–795 °C and 6.7–7.8 kbar. Pressure-temperature estimates for Cpx (rim)/GADS are significantly lower (between 685–740 °C and 6.6–7.2 kbar). Six calibrations (Kleeman and Reinhardt, 1994 and references therein) were used to determine Grt (core)-Bt temperatures. Whereas considerable scatter was observed (710–840  $^{\circ}$ C), none of the calibrations indicates a peak temperature close to that of the Opx–Cpx thermometers. Furthermore, no significant difference of the Grt-Cpx thermometer between the calibrations of Ellis and Green (1979) and Sengupta et al. (1989) was observed.

	Temperature (°C)	Pressure (kbar)
Grt-Bt/GADS		
Dasgupta et al. (1992) and Eckert et al. (1991)		
garnet core	774-840 (820 ± 20)	7.6-8.3 (8.1 ± 0.2)
garnet rim	685-821 (776 ± 40)	6.7 - 8.1 (7.6 ± 0.4)
Grt-Cpx/GADS		
Sengupta et al. (1989) and Eckert et al. (1991)	686–738 (715 ± 20)	6.7-7.2 ( $6.9 \pm 0.2$ )
Opx-Cpx/GADS		
Brey and Köhler (1990) and Eckert et al. 1991	866–889 (875 ± 20)	$\begin{array}{c} 8.9 - 9.1 \\ (9.0 \pm 0.1) \end{array}$

Table 2. Results of thermobarometry calculations for granulites from Rupaha, Sri Lanka



Fig. 4. Summary of the results of ion-exchange thermobarometry of granulites at Rupaha, Sri Lanka combined with garnet-clinopyroxene-plagioclase-quartz (GADS) barometry

The fluid composition of charnockitic rocks can be calculated from the model buffering reactions of  $2\text{Tr} = 4\text{Di} + 3\text{En} + 2\text{Qtz} + 2\text{H}_2\text{O}$  and  $2\text{Ann} + 6\text{Qtz} = 3\text{Fs} + 3\text{San} + 2\text{H}_2\text{O}$  (*Lamb* and *Valley*, 1988). The thermodynamic database of *Holland* and *Powell* (1998) was used together with the activity model for Caamphiboles of *Holland* and *Blundy* (1994). The activity of anorthite was calculated after *Holland* and *Powell* (1992), whereas the sanidine activity in K-feldspar as well as the enstatite and ferrosilite activities in Opx were obtained following *Holland* and *Powell* (1996). The calculated water activity is in the range of 0.05–0.09, indicating a very low activity of water during metamorphism.

The results of thermobarometry of our study compare well with the P–T estimates of other areas of the Highland Complex. *Schumacher* and *Faulhaber* (1994) estimated the P–T condition of the Eastern, North-eastern and South-eastern part of the Highland Complex at 760–830 °C and 9–10 kbar. *Sandiford* et al. (1988) used Gt–Cpx and Gt–Opx thermometry to illustrate the minimum temperature of metamorphism to be 670–730 °C. They noted that the actual peak metamorphism could easily be much higher. *Kriegsman* (1993) obtained peak equilibrium temperatures for sapphirine-bearing granulites in the Highland Complex at 830 °C and 9 kbar using petrogenetic grids. *Schenk* et al. (1988) derived a maximum temperature of 900 °C from two-pyroxene thermometry in the Highland Complex. *Voll* et al. (1994) estimated the peak temperatures of metamorphism between 850–900 °C using revised two-feldspar thermometry.

# Interdiffusion of elements during slow cooling

Fe–Mg zoning patterns in garnet caused by inter-diffusion between e.g., garnet– biotite or garnet–pyroxene, can be used to calculate the cooling history of the rock. A number of experimentally derived values for diffusion of Fe and Mg in garnet have been published (e.g., *Cygan* and *Lasaga*, 1985; *Ganguly* et al., 1998). *Ganguly* et al. (1998) determined diffusion coefficients at 1057–1400 °C by using almandine-pyrope diffusion couple experiments which were extrapolated down to the temperatures required for the modeling of this study. Since garnets from the Sri Lankan samples are almandine rich the most recent Fe–Mg diffusion coefficients determined by *Ganguly* et al. (1998) were used.

The diffusion of Ca and Mg in Mg-rich pyroxene is even slower by over 2 orders of magnitude. Similar inter-diffusion rates of Fe and Mg have been observed in pyroxenes and garnets (*Ganguly* and *Tazzoli*, 1994; *Ghose* and *Ganguly*, 1982), whereas Fe–Mg diffusion is much faster in biotite. Thus, biotites will re-equilibrate further during cooling than garnets. As a consequence, the obtained temperature from garnet core – biotite thermometry yields temperatures, which are difficult to interpret. These reset temperatures are '*apparent temperatures*' (e.g., *Florence* and *Spear*, 1995 and references therein), since they correspond to neither closure temperature nor equilibrium peak temperature.

In summary, the two-pyroxene thermometer records peak or near peak temperatures at Rupaha around  $875 \pm 20$  °C, whereas garnet–biotite thermometry yielded a much larger variation between 840–685 °C. We infer that this wide variation may be due to slow cooling of the terrane. In the following sections, we will quantify this interpretation using Fe–Mg profiles of garnet.

The evaluation of P–T conditions and the cooling history depends on the used grain size and the sectioning effect of minerals (*Ehlers* et al., 1994). Figure 2 shows backscattered images of garnets with surrounding matrix. The chemical compositions of garnets were analyzed along the shown lines (garnet/biotite, garnet/plagioclase and garnet/Cpx interfaces) (Fig. 3). The core compositions of the individual garnet grains are almost identical and are virtually independent of grain sizes (Fig. 3). Only very few small grains show a slightly different chemical composition which is most likely the result of sectioning, e.g., if a larger garnet is cut at the edge. In order to confirm this interpretation, the grain size of analyzed garnets is plotted against the temperature estimates from garnet-biotite thermometry in Fig. 5. Although there is a considerable range in obtained temperatures by garnet-biotite thermometry, most of the temperature estimates cluster around 820 °C for different grain sizes. Thus, sectioning effects can be neglected and we can assume that most garnet grains were cut across the homogeneous part of the garnet.

# Determination of cooling rates from garnet profiles

The Fe–Mg profiles in garnet are homogenous throughout most of the crystal. There is an increase in Fe and decrease in Mg at the rim (Fig. 3). The homogenous composition of most of the garnet crystal indicates a complete resetting or recrystallization of garnet during peak of metamorphism. We conclude that garnet exchanged fully with its surroundings at high temperatures. At lower T, diffusion



Fig. 5. Temperature estimates from garnet-biotite thermometry plotted against apparent grain sizes of garnets in thin section. Most temperature estimates cluster around 820 °C

in garnet is significantly slower and local exchange of Fe/Mg between adjacent grains results only in small Fe-Mg zoning at the rims.

### Retrieving the peak mineral chemistry

Since all of the garnet as well as the other Fe–Mg phases (biotite, clinopyroxene) in the matrix changed their composition in the first cooling step, we first attempt to retrieve the composition of the Fe–Mg minerals at peak temperature and pressure. This was accomplished by using the modal abundances of garnet, biotite and clinopyroxene (Grt = 47.8 vol.%, Bt = 27.2 vol.%, Cpx = 7.4 vol.%) to calculate the bulk Fe–Mg of the rock. The equilibrium equations between garnet, biotite and clinopyroxene were solved for Fe–Mg using this bulk composition at 875 °C and 9 kbar. This was achieved by simultaneously solving the mass balance- (Eqs. 1–4) and equilibrium coefficient equations (Eqs. 5–6) for Fe and Mg exchange. For these calculations it was assumed that no mineral growth or resorbtion (net transfer reaction) occurred during cooling. This assumption is supported by the fact that no retrograde growth of any high temperature phases can be observed in the studied samples. However, the slight increase in Mn in garnet rims indicates the consumption of garnet, but it is almost negligible compared to the Fe and Mg profile.

Mass balance is described by:

$$n_{\rm Fe}^{\rm tot} = m_{\rm Grt} * n_{\rm Fe}^{\rm Grt} + m_{\rm Bt} * n_{\rm Fe}^{\rm Bt} + m_{\rm Cpx} * n_{\rm Fe}^{\rm Cpx}$$
(1)

$$n_{Mg}^{\text{tot}} = m_{\text{Grt}} * n_{\text{Mg}}^{\text{Grt}} + m_{\text{Bt}} * n_{\text{Mg}}^{\text{Bt}} + m_{\text{Cpx}} * n_{\text{Mg}}^{\text{Cpx}}$$
(2)

$$n_{\rm Fe}^{\rm Bt} + n_{\rm Mg}^{\rm Bt} = \text{constant 1} \tag{3}$$

$$n_{\rm Fe}^{\rm Cpx} + n_{\rm Mg}^{\rm Cpx} = {\rm constant} \ 2$$
 (4)

	Peak temperature calculated 875	Apparent temperature core <b>820</b>	Reset temperature rim 685
Garnet			
Fe	1.503	1.528	1.605
Mg	0.670	0.645	0.479
Fe/(Fe + Mg)	0.692	0.703	0.770
Mg/(Fe + Mg)	0.308	0.297	0.230
Biotite			
Fe	1.070	0.932	0.928
Mg	1.490	1.560	1.590
Fe/(Fe + Mg)	0.418	0.374	0.369
Mg/(Fe + Mg)	0.582	0.626	0.631
Clinopyroxene			
Fe	0.341	0.311	0.311
Mg	0.697	0.727	0.727
Fe/(Fe + Mg)	0.329	0.300	0.300
Mg/(Fe + Mg)	0.671	0.700	0.700

Table 3. Recalculated peak composition and measured composition of garnet and biotite

where;  $n_i^{\text{tot}}$  is the total number of moles in species *i*; *i* = Fe, Mg,  $m_j$  is the number of moles of phase *j*; *j* = garnet, biotite, clinopyroxene and  $n_i^j$  is the number of moles of species *i* in phase *j*. Using these equations, it is possible to calculate the number of moles of garnet and biotite present in the system from the molar volumes and the modal amounts of these phases. The distribution coefficient (K<sub>d</sub>) of Fe and Mg between co-existing garnet-biotite and garnet-Cpx is described by:

$$K_{d}^{(Grt-Bt)} = \frac{(X_{Mg}/X_{Fe})^{Grt}}{(X_{Mg}/X_{Fe})^{Bt}}$$
(5)

$$K_{d}^{(Grt-Cpx)} = \frac{(X_{Mg}/X_{Fe})^{Cpx}}{(X_{Mg}/X_{Fe})^{Grt}}$$
(6)

Using these equations, Fe and Mg values at the metamorphic peak were retrieved for garnet, biotite and clinopyroxene. Results are presented in Table 3.

#### Diffusion modeling

The chosen diffusion model is based on the mineral zonation patterns observed. During or near peak metamorphism garnets are homogeneously reset, whereas during the later stage only garnet adjacent to biotite shows appreciable zoning. Volume diffusion in garnet has to be reasonably fast (high T) in order to produce flat zoning patterns (e.g., *Nagy* and *Giletti*, 1986; *Farver* and *Yund*, 1991; *Eiler* et al., 1992, 1995). In that case, diffusional fluxes should be balanced in representative volumetric elements, which are large compared to individual grains. Nevertheless, clinopyroxene occurs only in small quantities, therefore the diffusive fluxes have been balanced only between garnet and biotite.

During the cooling period diffusion along grain boundaries was limited, so that garnet zoning only developed when it was in direct contact with biotite and the two minerals shared common grain boundaries. For this case we assumed a model, which describes binary inter-diffusion between garnet and adjacent biotite grains. For a further discussion of diffusive exchange modeling and the mathematical treatments see *Dodson* (1973), *Lasaga* (1983), *Eiler* et al. (1992), and *Florence* and *Spear* (1995).

The modal proportion of biotite is about 27% in rocks from Rupaha (Table 3). Since the modal abundance of biotite is not much larger compared to garnet, diffusive fluxes change the composition of both, biotite and garnet. Thus, the concept of an infinite reservoir of biotite (*Dodson*, 1973) cannot be applied and we used a finite difference approach to solve the resulting differential equations, mass action and flux balance equations. The interdiffusion coefficients of *Ganguly* et al. (1998) together with a computer code written by *Robl* and *Stüwe* (2002) were used. Modal abundances of the rock used as input parameters for the calculation are: Grt = 48 vol.% and Bt = 27 vol.%. Two representative garnet grains with diameters of 660 and 460 µm have been modeled. Both, garnet and biotite are assumed to be homogeneous at starting temperature (875 °C). We have calculated zoning profiles for linear cooling rates of 50, 10, and 1 °C/Ma for a starting temperature of 875 °C and end temperature of 500 °C (Fig. 6). At high cooling rates, mass transfer by diffusion is only accomplished over a short period of time



Fig. 6. Comparisons of calculated Mg/(Mg + Fe) profiles with different cooling rates and measured Mg/(Fe + Mg): **a** profile A–B and **b** profile C–D from Figs. 2,3. The best-fit model assumes a slow cooling rate of 1-5 °C/Ma

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and garnet/biotite compositions change only slightly. Only the outermost rims are able to be in equilibrium with biotite at the given temperature all the time. Therefore the slope of the  $X_{Mg}$  curve at the garnet rim is steep (Fig. 6). Slower cooling rates enhance Fe–Mg exchange between garnet and biotite. Hence,  $X_{Mg}$  of garnet and biotite show its lowest and highest values, respectively and the slope of the  $X_{Mg}$  curve at the rim is less steep. The analysed garnet profiles are consistent with the calculated profiles for cooling rates between 1 and 10 °C/Ma, most likely around 1–5 °C/Ma (Fig. 6).

# **Discussion and conclusions**

This work attempts to show that compositional zoning in garnet from Sri Lankan granulite facies rocks can be used to support a slow cooling history of the central Highland basement Complex. We manage to retrieve a cooling history which is consistent with other geological constraints. Ca–Fe–Mg exchange thermobarometry of co-existing Opx–Cpx and Grt–Cpx–Pl–Qtz is consistent with calculated P–T phase diagrams for the rocks of the Rupaha area (*Kriegsman*, 1993). They indicate that peak metamorphism occurred at  $875 \pm 20$  °C and  $9.0 \pm 0.1$  kbar. However, Fe–Mg exchange thermometry of Grt (core)–Bt gives temperatures around  $820 \pm 20$  °C. From the results presented from different mineral pairs, we made it clear that compositions from garnet corresponding to maximum temperature are reset whereas compositions of pyroxene have been preserved longer.

A low water activity ( $\leq 0.1$ ), has been estimated by two fluid buffering equilibria inferred from charnockitic rocks. We therefore conclude that only a limited amount of fluid phase was available in order to transport elements by grain boundary diffusion. However, the homogeneous resetting of garnet composition during the peak of metamorphism or initial stage of cooling indicates that grain boundary diffusion was taking place to some extent. Garnet zoning pattern and two dimensional compositional maps reveal that zoning occurred only at garnet–biotite contacts. This also suggests a lack of fluid during this stage and a very local Fe–Mg exchange. Our conclusion of lack of fluid is supported by the absence of retrograde mineral reactions in the rocks.

U–Pb zircon dating of syntectonic granitoids in the Highland Complex yielded an age of  $608 \pm 3$  Ma (*Hölzl* et al., 1991) which is interpreted as the timing of peak metamorphism. The cooling history of the basement rocks started with a cooling rate of 1-5 °C/Ma at  $608 \pm 3$  Ma, 875 °C and 9 kbar. During this early period diffusion in garnet is fast and garnets are homogenously reset. Further cooling to lower temperatures at about the same cooling rate of 1-5 °C/Ma reduced volume diffusion in garnet producing the retrograde rims observed in garnet. The deduced slow cooling rate indicates a prolonged crustal residence time and slow ascent of this basement unit. This slow ascent can be explained as consequence of erosion at the surface and isostatic compensation. A Rb–Sr biotite age of  $439 \pm 10$  Ma (*Hölzl* et al., 1991), which is believed to record the time at temperatures around  $300 \pm 30$  °C (*Spear*, 1993), indicates the final cooling during the exhumation of the basement.

Radiometric age data available for Sri Lankan metamorphic rocks allow a comparison with our results (Fig. 7). *Hölzl* et al. (1991) proposed a two stage



Fig. 7. Calculated cooling paths of granulites from Sri Lanka from this study compared with cooling rates inferred from geochronology (*Hölzl* et al., 1991). Their U–Pb zircon age of  $608 \pm 3$  Ma was assumed to represent the age of peak metamorphism in this study

cooling history based on Sm–Nd garnet ages and Rb–Sr biotite ages for rocks from the Highland Complex. A cooling rate of 2 to  $3 \degree C/Ma$  was deduced from garnet followed by a significantly higher cooling rate of around 10 to  $25 \degree C/Ma$  deduced from biotite ages. Cooling rates determined by diffusion profiles in garnet do not require the two stage process as suggested by *Hölzl* et al. (1991). However, a single stage cooling history with similar cooling rates can be inferred from geochronolgy by reinterpreting the data of *Hölzl* et al. (1991). They used for their cooling rate calculations a blocking temperature of garnet at about 800 °C, which is significantly higher than proposed by *Mezger* et al. (1992). *Mezger* et al. (1992) reported that the closure temperature for Sm–Nd exchange in garnet can be significantly lower than 800 °C, most likely at around 600 °C.

However, cooling rates determined by diffusion profiles depend on the used diffusion coefficients. The diffusion coefficients given by different authors (*Cygan* and *Lasaga*, 1985; *Ganguly* et al., 1998 and references therein) and the uncertainties in diffusion coefficients have a large influence on the calculated zoning profiles and thus on the calculated cooling rate. Reducing or enlarging the diffusion coefficients leads to slower or faster cooling rates, respectively. The used diffusion coefficients of Fe and Mg in garnet determined by *Ganguly* et al. (1998) are consistent with the observed garnet zonation pattern reflecting a slow cooling history, which is supported by geochronolgical data.

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