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MELTING CARBONIC FLUIDS AND  
WATER RECYCLING IN THE DEEP CRUST:  
AN EXAMPLE FROM THE LIMPOPO BELT,  
SOUTH AFRICA

**GARY STEVENS**

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**INFORMATION CIRCULAR No. 290**

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CRUST: AN EXAMPLE FROM THE LIMPOPO BELT, SOUTH AFRICA**

**by**

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## ABSTRACT

The proposed retrograde orthoamphibole isograd in the Southern Marginal Zone of the Limpopo Belt separates hydrated, amphibolite-grade metapelites from their granulite-grade precursors. This feature provides an intriguing geological dilemma. The widespread rehydration of metapelitic granulites under conditions of approximately 660 to 600 °C and > 0.6 GPa, as well as CO<sub>2</sub>-dominated fluid-inclusion populations in a terrane where carbonate rocks are absent, appear to suggest thorough flushing of a large volume of high-grade crust with an externally derived low *a*H<sub>2</sub>O (CO<sub>2</sub>-rich) fluid. However, past studies of the carbon and oxygen isotope geochemistry of the hydrated rocks have not demonstrated the involvement of any voluminous “out of equilibrium” fluid phase in the evolution of the rocks.

This contribution, based on data from both amphibolite- and granulite-grade exposures, proposes a model wherein the hydrating fluids are derived from crystallising anatetic leucosomes, which were generated by *in-situ* fluid-absent biotite melting along the prograde path. Model equilibrium fluid compositions suggest that reaction between this melt-derived H<sub>2</sub>O and biogenic graphite produced fluid:rock ratios potentially as high as 1:5 at the wet granite solidus. At this time, the presence of graphite would have buffered XH<sub>2</sub>O to low values, for all reasonable estimates of *f*O<sub>2</sub>. There is thus no need to invoke the involvement of externally derived fluid. Declining temperature would, however, have resulted in fluid compositions shifting to higher XH<sub>2</sub>O, with the precipitation of graphite essentially at the sites of initial fluid generation, thereby preserving original (pre-metamorphic) isotopic heterogeneities.

The hydration pattern of the Southern Marginal Zone is largely a function of melt migration. In the hydrated zone, leucosomes generally approximate minimum melt compositions. In contrast, leucosomes in the granulite-grade portion of the terrane have the mineralogical character of quartz, plagioclase cumulates, having lost a K<sub>2</sub>O- H<sub>2</sub>O-rich melt fraction. In a general context, *in situ* crystallisation of graphitic partially-melted source rocks has the potential to produce high fluid-rock ratios at temperatures close to the wet granite solidus. This single process holds the potential for widespread retrogression of formerly high-grade assemblages, at a variety of *a*H<sub>2</sub>O values, without external fluid input. Channellisation and evacuation of this fluid along deformation zones will inevitably lead to the intense alteration and possible mineralisation of associated rocks, as in the Limpopo Belt.

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# MELTING, CARBONIC FLUIDS AND WATER RECYCLING IN THE DEEP CRUST: AN EXAMPLE FROM THE LIMPOPO BELT, SOUTH AFRICA

## INTRODUCTION

The involvement of fluids and melts are inextricably linked in the history of many high-grade crustal rocks. Subsolidus dehydration reactions are unlikely in the quartzofeldspathic crust at metamorphic grades in excess of mid-amphibolite facies, as under these conditions hydrous silicates generally breakdown by  $H_2O$ -conserving incongruent melting reactions (Brown and Fyfe, 1970; Fyfe, 1973; Clemens, 1990; Stevens and Clemens, 1993). Melt segregation following such anatetic reactions is a powerful agent for the concentration of  $H_2O$  and lithophile elements that are strongly compatible in the melt (K, Th, Ta, Nb, LREEs, Sn, F, Au, U, etc.). In cases where melt migration is possible and efficient, the melt leaves the high-grade environment and a degree of crustal differentiation is achieved (Vielzeuf *et al.*, 1990). However, many granulites do not have the chemical character of melt-depleted restites and are often migmatised. In these cases a melt component has remained trapped in the high-grade source throughout the granulite-grade and subsequent cooling history. In this scenario some degree of retrograde reaction between the granulite-grade, anhydrous, restitic assemblage and the melt borne  $H_2O$  component is inevitable during the cooling history (Ashworth, 1985; Ashworth and McLellan, 1985; Waters, 1988). A degree of retrograde overprinting is thus to be expected in migmatitic granulites where an anatetic history is inferred.

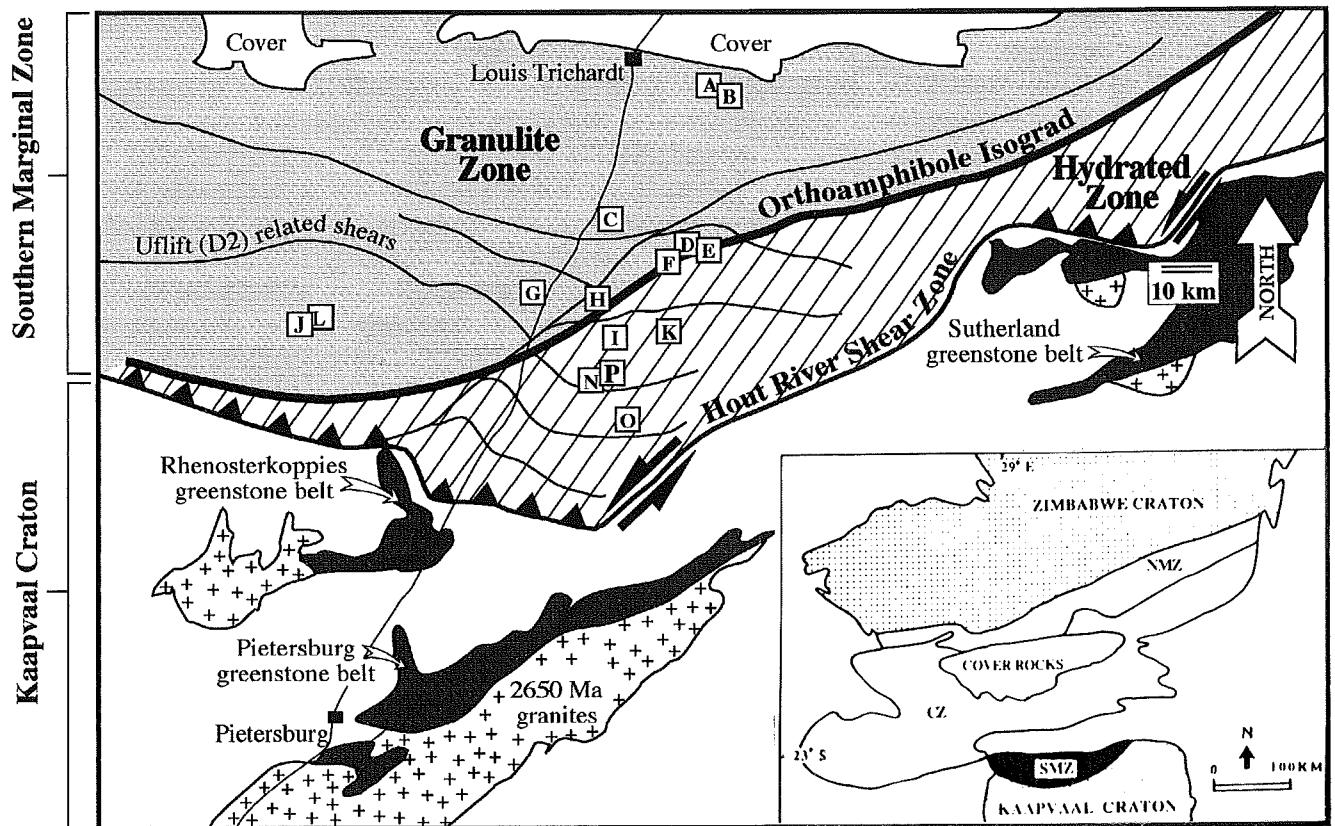
In this paper, data are presented from metapelites exposed in the Southern Marginal Zone (SMZ) of the Archaean Limpopo Belt of South Africa (Fig. 1) that provide potentially valuable insights into these processes of retrograde fluid-melt-rock interaction in the partially-melted, high-grade crust. This study aims to show that; (1) the degree of hydration in the SMZ correlates with the degree to which melt was retained in the system during the peak of metamorphism; (2) fluid abundance during the crystallisation of *in-situ* anatetic leucosomes was enhanced by simultaneous oxidation of graphite; (3) the comprehensive hydration of the rocks occurred over a relatively narrow temperature interval that coincides with the evolution of the terrane through the  $H_2O$ -saturated granite solidus; and, (4) orthoamphibole is not a stable phase in the final hydration assemblage in the rocks examined in this study.

## GEOLOGICAL SETTING AND PREVIOUS WORK

The Limpopo Belt crops out as a narrow band of E-W trending high-grade metamorphic rocks along the South Africa - Zimbabwe - Botswana borders (Fig. 1). The belt can be subdivided into a Central Zone and a Northern and a Southern Marginal Zone, all at granulite grade. The Central Zone consists mainly of epicontinental rocks, whereas the two marginal zones consist primarily of the deformed, attenuated and ultra-metamorphosed equivalents of the granite-greenstone successions of the bounding Zimbabwe and Kaapvaal cratons (Du Toit *et al.*, 1983; Van Reenen *et al.*, 1990).

The metapelitic migmatites discussed in this study are all located in the Southern Marginal Zone (SMZ). Here, the tonalitic to trondhjemite grey gneiss of the craton is represented by the migmatised Bavianskloof Gneiss, and the greenstones of the craton have been transformed into the granulite-grade, pelitic, mafic and ultramafic units of the Bandelierkop Formation (Du Toit *et al.*, 1983) (Fig. 1). The metapelites are of variable composition, having  $Mg\#s$  ( $100 \cdot Mg/(Mg + Fe)$ ) between 50 and 80. The rocks also show variable degrees of alumina saturation, with only a small proportion having evidence of sillimanite in the prograde assemblage. In general, these rocks are magnesian, with relatively high  $MgO + FeO$  and low  $K_2O$  and  $Al_2O_3$  compared to typical modern sedimentary rocks (Table 1). The metasediments of the Bandelierkop

Formation are compositionally homogeneous over the entire SMZ (Van Reenen, 1983). This probably rules out a metasomatic origin for the magnesian nature of these rocks. A more likely scenario is that of sedimentation in an environment of active ultramafic magmatism, thereby enriching the sediments in  $MgO + FeO$  while raising the  $Mg\#$  through the addition of an ultramafic tuffaceous component. The incorporation of a mafic component is unlikely as the metasediments with the highest  $Mg\#s$  are not characterised by high  $CaO$  contents (Table 1).



*Figure 1: The geology of the Southern Marginal Zone of the Limpopo Belt modified after Van Reenen et al. (1989). Note the tectonic contact between the low-grade rocks of the Kaapvaal Craton and rocks formerly at granulite-grade, and the broad band of hydration between the retrograde orthoamphibole isograd and the Hout River Shear Zone. The sample localities of the present study are indicated on the map. Decompression of the terrane was achieved through uplift on the D2 shear zones that dip steeply to the north (Van Reenen et al., 1989).*

**Table 1: Representative Bandelierkop Formation metasediment bulk-compositions. (a) Granulite-grade samples. GGn - examples of relatively Fe-rich garnet gneiss in which the reaction  $\text{Grt} + \text{Qtz} = \text{Crd} + \text{Opx}$  has not occurred, GCGn - examples of garnet-cordierite gneiss in which the reaction has occurred but has not run to completion, CGn is an example of a cordierite gneiss in which the reaction has run to completion, PM is an example of the most Mg-rich compositions. The average shale composition (Sh) of Shaw (1956) and the average metagreywacke (Gw) of Pettijohn (1963) are also listed for comparison. (b) Compositions associated with the hydrated zone of the SMZ. N12, I7 and K7b are from within the zone of hydration; DV3, F19 and D22 are from the vicinity of the orthoamphibole isograd. All these rocks contain cordierite, although some of the Mg#s suggest that in the granulite zone they would not ( $\text{Mg\#} < 65$ ). Data presented on DV3 are from Van Reenen (1986)**

**(a)**

Wt%	GGn		GCGn		CGn	PM		
	C3	A15	C7	H6	C17	C9	Sh	Gw
$\text{SiO}_2$	65.19	62.49	57.24	58.60	56.07	54.01	64.84	70.35
$\text{TiO}_2$	0.48	0.84	0.88	0.73	0.65	0.57	0.86	na
$\text{Al}_2\text{O}_3$	17.08	16.26	18.95	14.59	18.74	16.15	17.86	14.24
$\text{Fe}_2\text{O}_3$	1.45	na	1.12	na	0.32	3.08	na	na
$\text{FeO}$	3.05	7.64	7.04	9.09	7.54	6.20	6.35	5.38
$\text{MnO}$	0.07	0.15	0.07	0.19	0.07	0.14	0.00	0.00
$\text{MgO}$	3.13	7.06	8.79	9.81	10.78	14.7	2.66	2.22
$\text{CaO}$	5.38	1.34	1.57	2.95	1.92	2.16	1.85	2.64
$\text{Na}_2\text{O}$	3.31	1.77	1.42	2.47	1.75	1.82	1.93	3.06
$\text{K}_2\text{O}$	0.86	2.11	2.95	1.32	1.52	1.15	3.64	2.11
<b>Total</b>	100.00	99.76	100.03	99.83	99.36	99.98	99.99	100.00
<b>Mg#</b>	64	61	69	66	72	81	43	43

**(b)**

Wt%	GCGn					CGN
	DV3	I7	K7b	F19	D22	N12
$\text{SiO}_2$	65.20	60.70	58.66	65.74	58.16	57.54
$\text{TiO}_2$	0.68	0.66	0.63	0.53	0.77	0.73
$\text{Al}_2\text{O}_3$	13.70	14.69	15.93	13.90	15.79	16.34
$\text{Fe}_2\text{O}_3$	0.88	na	na	na	na	na
$\text{FeO}$	7.92	9.02	8.82	6.39	9.93	7.45
$\text{MnO}$	0.08	0.17	0.13	0.16	0.15	0.07
$\text{MgO}$	6.3	9.72	11.32	6.49	8.10	11.96
$\text{CaO}$	1.39	1.54	1.26	1.73	1.59	2.22
$\text{Na}_2\text{O}$	1.80	1.49	0.88	2.25	2.85	2.07
$\text{K}_2\text{O}$	1.82	1.74	2.18	2.47	2.39	1.62
<b>Total</b>	99.77	99.73	99.92	99.78	99.85	100.00
<b>Mg#</b>	59	66	69	64	59	74

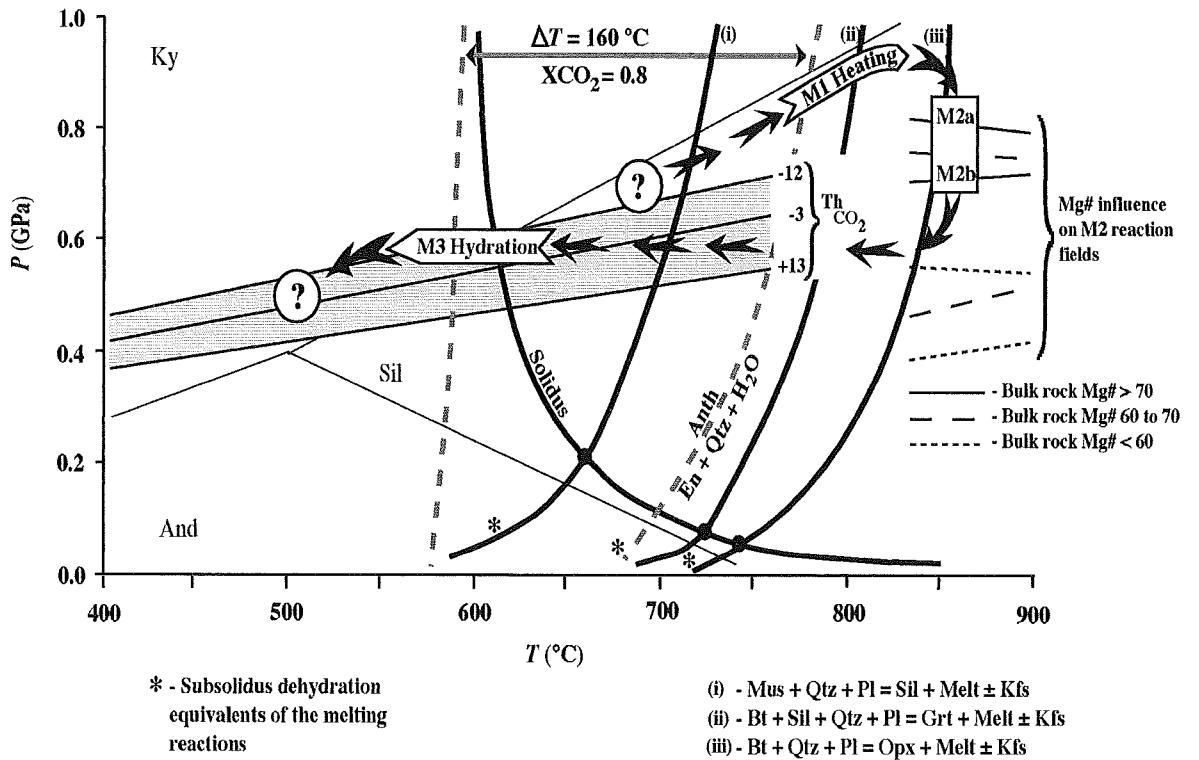
Previous studies on the metamorphism of SMZ metapelites have described a clockwise  $P$ - $T$  loop (Fig. 2) that is based on the identification of relic reaction textures used as “fossil geothermobarometers” (e.g. Frost and Chacko, 1989). The key elements in this data are: 1) new generations of anhydrous phases associated with several generations of anatetic leucosome, which allow identification of the fluid-absent melting reactions,  $\text{Ms} + \text{Qtz} + \text{Pl} = \text{Sil} + \text{Melt} \pm \text{Kfs}$ ,  $\text{Bt} + \text{Sil} + \text{Qtz} + \text{Pl} = \text{Grt} + \text{Melt} \pm \text{Kfs}$ ,  $\text{Bt} + \text{Qtz} + \text{Pl} = \text{Grt} + \text{Opx} + \text{Melt} \pm$

Kfs and,  $Bt + Qtz + Pl = Opx + Crd + Melt \pm Kfs$  (Stevens and Van Reenen, 1992a). These reactions occurred during a period of prograde heating (M1) in the sillimanite stability field (Stevens and Van Reenen, 1992b); 2) cordierite replacement of garnet and sillimanite, and cordierite-orthopyroxene symplectic replacements of garnet that indicate a period of decompression at high grade (M2a and M2b respectively) (Van Reenen, 1983; Stevens and Van Reenen, 1992b), and; 3) hydration textures, consuming cordierite and orthopyroxene, that produce kyanite in rocks where biotite-garnet thermometry indicates retrograde temperatures of  $\sim 600$  °C (Van Reenen, 1986). The period of isobaric cooling at  $P \geq 0.6$  GPa between the end of decompression and the beginning of hydration is supported by fluid-inclusion data (Van Reenen, 1986) and the absence of decompression reactions in the most Fe-rich metasediments (Stevens and Van Reenen, 1992b).

The widespread hydration of rocks in the southern portion of the SMZ that were formerly at granulite-grade was first described by Van Reenen (1986). The identification of a well defined transition zone separating granulite-grade rocks in the north from a hydrated zone in the southern portion of the SMZ, where orthopyroxene is not preserved, resulted in the erection of a retrograde orthoamphibole isograd (Fig. 1).  $CO_2$ -rich fluid inclusion compositions (Van Reenen and Hollister, 1987) and the apparent displacement of the reaction  $Opx + Fl + Qtz = Anth$ , to temperatures of approximately 600 °C, in the kyanite stability field (Fig. 2) led Van Reenen and Hollister to suggest the pervasive flushing of this portion of the deep Archaean crust with a  $CO_2$ -dominated retrograde fluid. The presence of an  $H_2O$ -undersaturated fluid during the retrograde history of the SMZ has been confirmed by a study of the retrogression in the associated ultramafic unit of the Bandedierkop Formation (Van Schalkwyk and Van Reenen, 1992), and has also been suggested by a phase-equilibrium study by Baker *et al.* (1992).

The findings of these studies appear inequitable with two other lines of evidence. Firstly, in a study of the stable isotope geochemistry of rocks from both the granulite zone and the hydrated zone Venneman and Smith (1992) observed that  $\delta^{13}C$  values in the graphitic metasediments varied by 5 to 6 ‰ on a layer scale (metres). Also, original  $^{18}O/^{16}O$  ratios were generally preserved between different rock types. Thus, the stable isotope systematics appear to rule out the equilibration of the rocks with a pervasive, externally-derived fluid of any composition. This finding is supported by  $\delta^{18}O$  data from a subsequent study of Hoernes and Van Reenen (1992), which also suggested that the bulk of the hydrated rocks have not equilibrated with a voluminous, externally-derived fluid. Secondly, an increasing body of experimental evidence on the physical interaction of minerals and fluids suggests that it is not possible for  $CO_2$ -dominated fluids to pervasively infiltrate the high-grade crust (Brennan and Watson, 1987; Watson and Brennan, 1987; Holness and Graham, 1991), and that the ingress of such fluids should be deformation controlled and strongly channelled (Fein *et al.*, 1994).

The findings of the present study provide a possible solution to this apparent discrepancy. During the petrographic investigation of samples collected at the localities illustrated in Figure 1, attention was focused on the widespread, but variable, nature of the retrograde overprint. Examples of all chemical varieties of the metasediments contain evidence of retrogression, in both the granulite and hydrated zones. The distinction between the two zones has been based on the preservation or destruction of orthopyroxene during the hydration episode (Van Reenen, 1986). Despite this, petrographic observations allow for the identification of a chronological sequence of retrograde reactions that is very similar in rocks from both north and south of the proposed retrograde isograd.



*Figure 2: The P-T loop for the SMZ proposed by Stevens and Van Reenen (1992b). The calculated fluid phase composition during retrogression, based on the displacement of the hydration reaction, is from Van Reenen (1986). The fluid-inclusion data are from Van Reenen and Hollister (1987).*

## PETROGRAPHY OF THE HYDRATION REACTIONS

### Granulite Zone

In the rocks retaining granulite-grade assemblages, several different mineral textural associations indicate retrograde reactions. Euhedral cordierite porphyroblasts in the leucosomes, and cordierite produced by decompression reactions and rimming garnet in the leucosomes and the metasediments, is partially replaced by biotite, kyanite and quartz (Fig. 3). Orthopyroxene, both in the leucosomes and in the metasediments, is partially replaced by coarse-grained biotite-quartz intergrowths. In the case of the replacement of orthopyroxene phenocrysts in the leucosomes, the quartz lamellae are commonly in optical continuity with large quartz crystals in the surrounding leucosome matrix. Both of these replacement textures, with biotite in the product, are only well developed in proximity to leucosomes. Thus, it appears that the initial stages of retrogression in the granulite zone occurred through water-conserving reactions, involving melt, i.e. (i)  $\text{Crd}^* + \text{Melt} = \text{Bt} + \text{Qtz} + \text{Ky}$  and (ii)  $\text{Opx} + \text{Melt} = \text{Bt} + \text{Qtz}$  (\*The mineral abbreviations used are those suggested by Kretz (1983), as well as Fl = fluid). These reactions would have occurred in response to rising  $a\text{H}_2\text{O}$  in the melt during the crystallisation of the leucosomes (Ashworth, 1985).

A third retrograde reaction can be inferred from the common occurrence of fine-grained, fibrous intergrowths of kyanite and orthoamphibole (The intergrowth is too fine-grained to obtain accurate mineral analyses. However, a detailed SEM investigation has proved the ferromagnesian product of the reaction to be Al-rich orthoamphibole) that partially replace cordierite remaining after reaction (i). This texture contrasts strongly with the products of reaction (i) and (ii) in that it is confined to grain boundaries (Fig. 4), probably indicating the involvement of a grain-boundary fluid film in the reaction i.e. (iii)  $\text{Crd} + \text{Fl} = \text{Ky} + \text{Oamp} + \text{Qtz}$ . The fibrous intergrowths are commonly associated with fine-grained graphite flakes, indicating carbon mobility, and further suggesting the involvement of a fluid in the development of these textures. The last piece of petrographic evidence indicating partial reaction during retrogression is the growth of a new generation of small euhedral garnet crystals (Fig. 4). These second-generation, euhedral garnets form only a fraction of the assemblage, but clearly overprint and contain inclusions of the kyanite-orthoamphibole intergrowth.

### At the Isograd

In the samples examined in this study from near the isograd the sequence of reactions is very similar to that described for the rocks to the north. The products of the crystallisation-hydration reactions (i) and (ii) are, however, more extensively developed (Fig. 5), and orthopyroxene appears to have been removed from the assemblage by reaction (ii). Van Reenen (1986), however, described a sample from the isograd (DV3) where orthopyroxene is rimmed by anthophyllite, indicating the reaction  $\text{Opx} + \text{Qtz} + \text{Fl} = \text{Anth}$  (iv). This is an orthopyroxene-consuming reaction analogous to reaction (iii) that is developed throughout the SMZ. Reaction (iii) has acted on the cordierite not consumed by reaction (i), converting it to a substantially more coarse grained intergrowth of kyanite and orthoamphibole than is produced in the granulite-zone. In these rocks the second generation of garnet is also much more extensive than in the previously described rocks. The late-stage garnet growth commonly occurs as overgrowth rims to the original poikilitic granulite-grade cores. The interfaces separating new garnet growth from old are often marked by small graphite flakes. As in the case of reaction (iii) in the granulite zone, this probably indicates fluid involvement in the reaction. As in the case of the granulite zone the garnet overgrowths often contain inclusions of the kyanite and orthoamphibole resulting from reaction (ii), suggesting that the garnet is produced by a reaction consuming these phases i.e.  $\text{Oamp} + \text{Ky} + (\text{K}_2\text{O}^* + \text{H}_2\text{O}) = \text{Grt} + \text{Bt} + \text{Qtz}$  (v) (\*A following discussion deals with the possible sources of potassium and  $\text{H}_2\text{O}$  in this reaction).

### Hydrated Zone

The reactions inferred from the petrography of the metasediments in the hydrated zone are identical to those already discussed. However, the degree of retrogression and the grain size of the reaction products are greater. In these rocks, very little cordierite or orthopyroxene remains, and the products of reactions (i), (ii) and (iii) are extensively developed. Reaction (v) has produced a substantial quantity of new garnet (Fig. 6). Due to the higher degree of reaction in these samples, garnet includes abundant relics of orthoamphibole and kyanite. Biotite and garnet produced by this reaction clearly replace orthoamphibole (Fig. 7). The new garnet generation contains inclusions of graphite (Fig. 6), again confirming the involvement of a fluid phase in the evolution of these relatively late textures. In these samples, rare crystals of orthopyroxene not consumed by reaction (ii) are never in contact with the assemblage, but exist as relic cores within anthophyllite, indicating the occurrence of reaction (iv) in these rocks. Representative compositions of phases associated with the hydration reactions in the granulite zone, at the isograd and in the hydrated zone are presented in Tables 2 to 5.

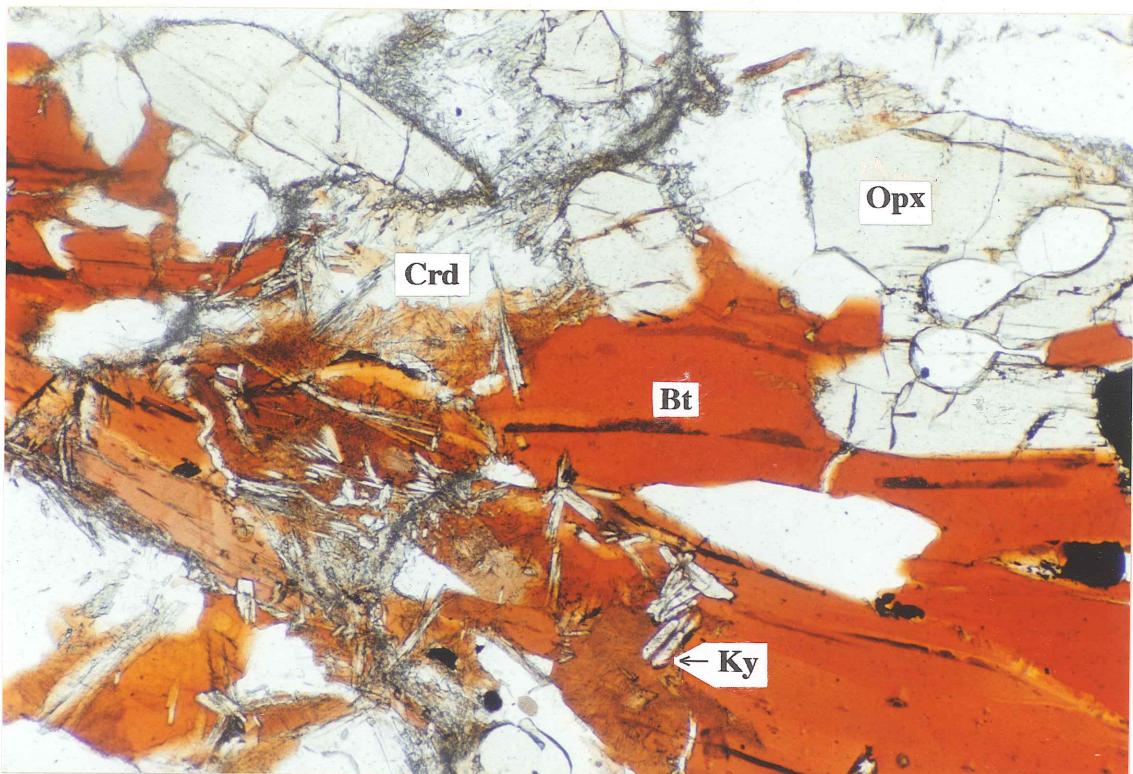


Figure 3: Photomicrograph illustrating the texture produced by the reaction  $\text{Crd} + \text{Melt} = \text{Bt} + \text{Ky} + \text{Qtz}$  (i) in the granulite zone.

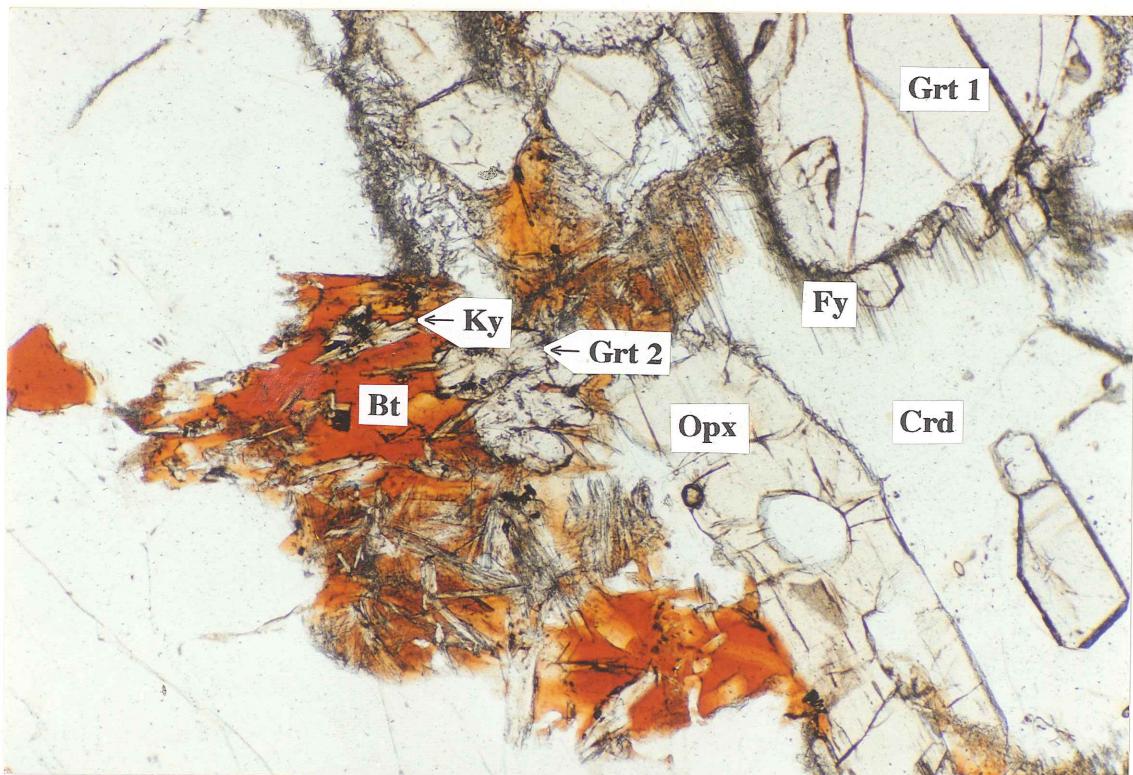


Figure 4: Photomicrograph illustrating the late replacement of cordierite by a fine-grained, fibrous intergrowth of kyanite and orthoamphibole. These reaction products are confined to grain boundaries and are often associated with graphite. Note the late generation of small euhedral garnet crystals that overprint the fibrous intergrowth and represent the last reaction recorded in these rocks.

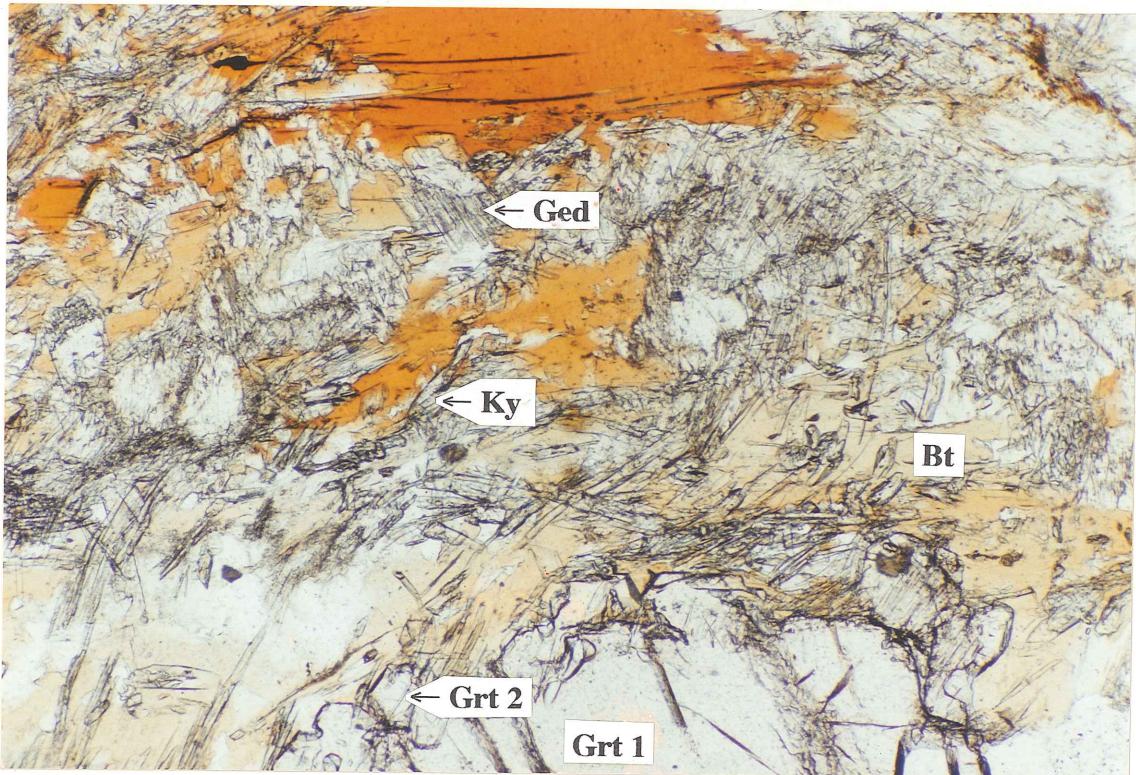


Figure 5: Photomicrograph illustrating the late replacement of cordierite in samples from the isograd by biotite and kyanite (reaction i) and by kyanite and orthoamphibole (reaction iii). Note the subsequent garnet growth, largely nucleated on the granulite-grade cores.

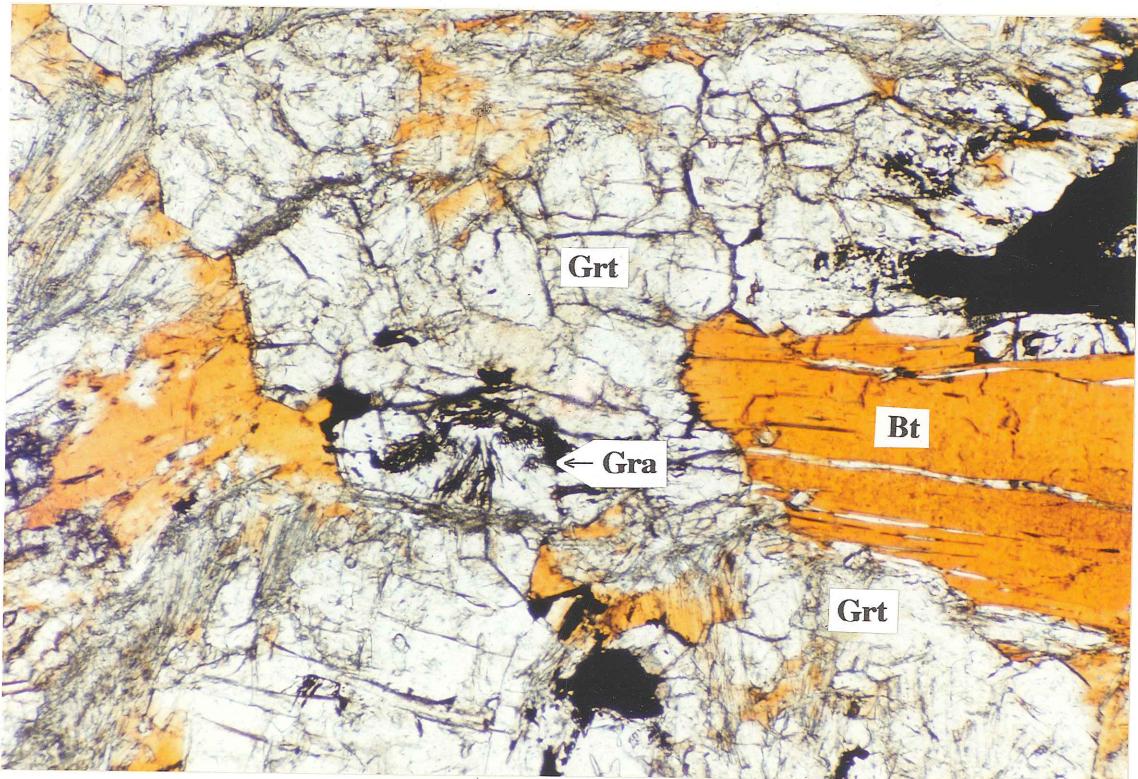


Figure 6: Photomicrograph of the retrograde textures in sample I7 from the hydrated zone. In these rocks new garnet growth is extensive and garnet contains inclusions of kyanite, orthoamphibole and graphite.

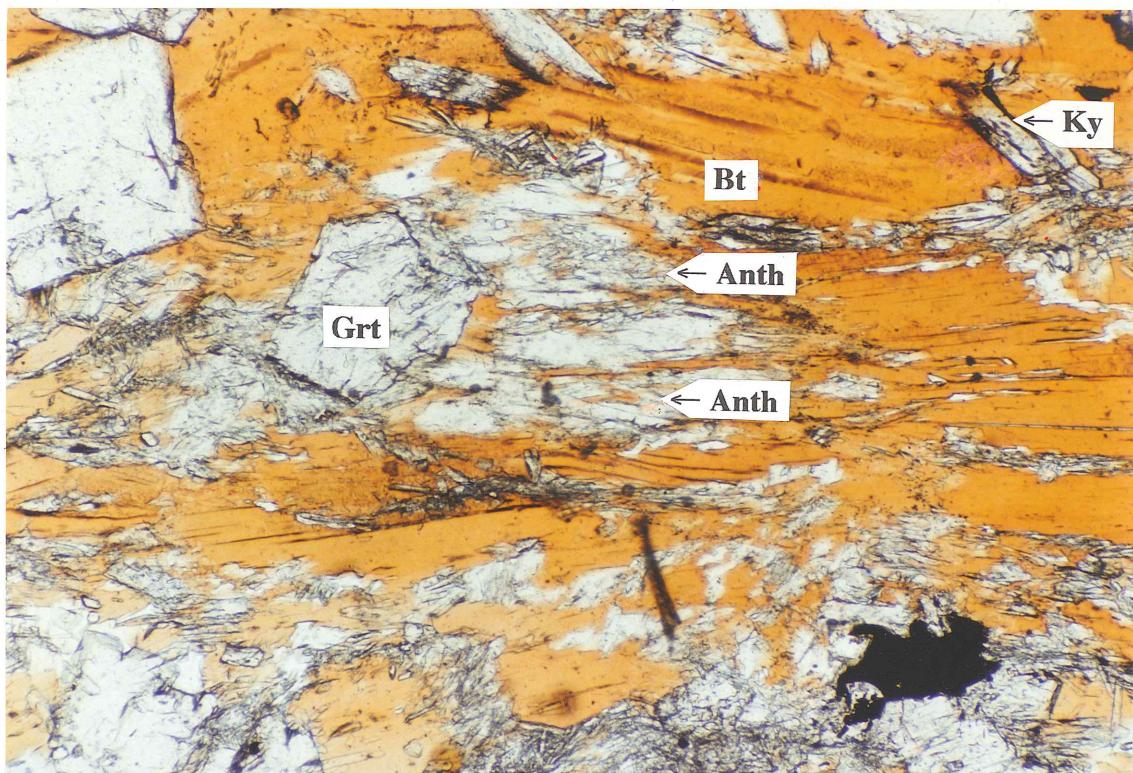


Figure 7: Photomicrograph of the retrograde textures in sample I7 from the hydrated zone. In these rocks, where degrees of retrogression are highest, there is clear textural evidence for the replacement of orthoamphibole by biotite.

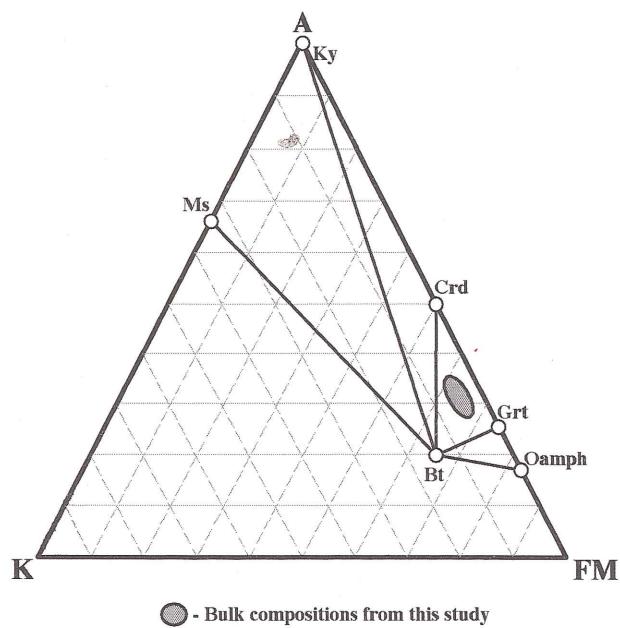


Figure 8: Representative hydrated zone bulk-rock and mineral compositions plotted on anA,K,FM projection addadapted from Arnold and Sandiford (1990). Apices are A:  $\text{Al}_2\text{O}_3$ , K:  $\text{K}_2\text{O}$ , FM:  $\text{FeO} + \text{MgO}$ . The projection is from plagioclase, quartz and fluid. The bulk compositions analysed in this study plot in the field Ky-Bt-Grt, consistent with the suggested production of orthoamphibole by a metastable, overstepped reaction, and the subsequent overprinting of orthoamphibole by the biotite-garnet assemblage.

## Summary

Retrogression in both zones appears to have been initiated by  $\text{H}_2\text{O}$  conserving crystallisation-hydration reactions that produced biotite and kyanite. These reactions were followed by further breakdown of cordierite in the granulite zone, and cordierite and orthopyroxene in the hydrated zone, as the system became fluid-present due to the leucosome melts becoming  $\text{H}_2\text{O}$ -saturated during the latter stages of crystallisation. These initial fluid-present reactions produced orthoamphibole, in rocks that appear to be too potasic and aluminous to contain orthoamphibole as an equilibrium phase with biotite, garnet and kyanite (Fig. 8). The final equilibrium recorded by the retrograde assemblages results from reaction (v) that consumes orthoamphibole and kyanite and produces new generations of garnet and biotite (Fig 9). In both zones the retrograde assemblages are characterised by incomplete reactions. The products and reactants of the numerous sequential hydration reactions are generally present in all samples. This argues for restricted fluid availability as the controlling factor in determining the degree of hydration and the preservation of disequilibrium features. An analysis of the leucosome compositions in the two zones provides a possible reason for the differences in fluid abundance.

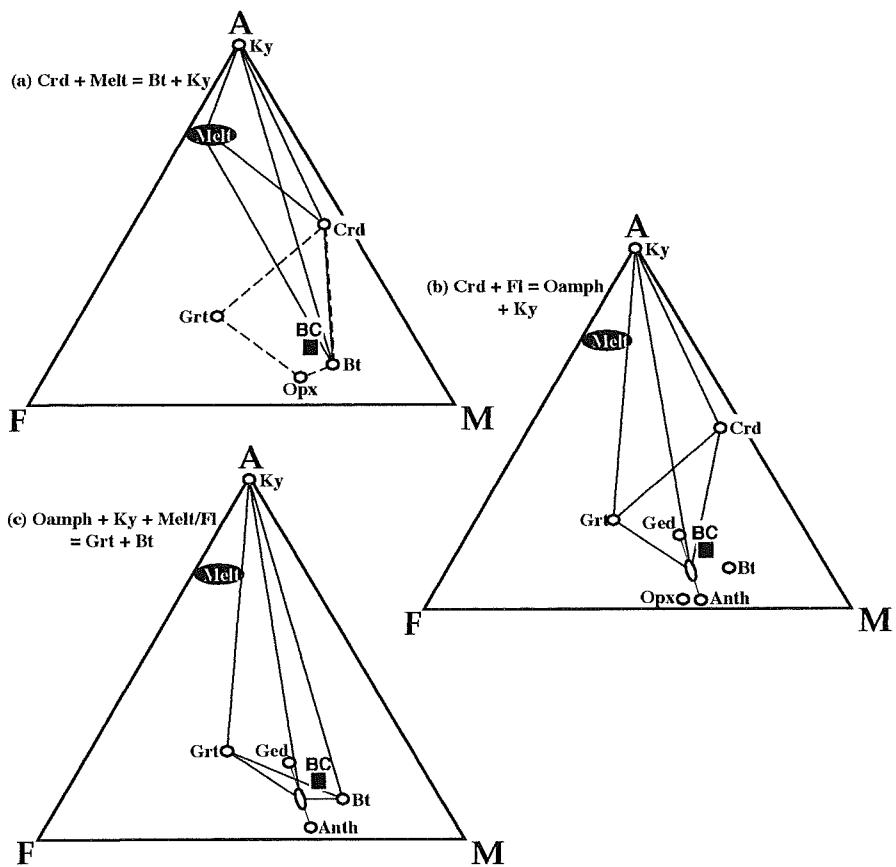


Figure 9: AFM plots for some of the retrograde equilibria proposed in this study. (a)  $\text{Crd} + \text{Melt} = \text{Ky} + \text{Bt}$ . Note that the granulite-grade assemblage  $\text{Grt} + \text{Opx}$  persists, introducing the disequilibrium assemblage (at 600 °C and 0.6 GPa)  $\text{Opx} + \text{Qtz} + \text{Ky}$ . (b)  $\text{Crd} + \text{Fl} = \text{Oamph} + \text{Ky} + \text{Qtz}$ . This reaction occurred through an overstepped equilibrium as the system became fluid-present in rocks that contained melt. (c) The final retrograde assemblage overprint in both zones resulted from the reaction  $\text{Oamph} + \text{Ky} + \text{Melt/Fl} = \text{Bt} + \text{Grt}$ .

**Table 2: Representative retrograde biotite compositions calculated to 22 oxygen. Compositions from the granulites are most likely to have equilibrated during reactions (i) and (ii). Those from the rocks at the isograd and from the hydrated zone most likely re-equilibrated during reaction (v)**

wt %	Granulite zone			At the isograd			Hydrated zone	
	C3a	C8d	H6	DV3	F19	D22	I7	K7b
<b>SiO<sub>2</sub></b>	37.08	37.95	37.91	36.81	37.36	37.12	37.97	37.71
<b>TiO<sub>2</sub></b>	4.04	4.78	3.70	3.63	3.00	2.54	2.68	3.05
<b>Al<sub>2</sub>O<sub>3</sub></b>	17.91	17.25	17.10	17.24	16.95	18.04	17.86	17.15
<b>Cr<sub>2</sub>O<sub>3</sub></b>	0.00	0.00	0.24	0.75	0.29	0.21	0.36	0.57
<b>FeO</b>	10.36	10.68	11.64	11.47	15.06	14.09	11.19	10.91
<b>MgO</b>	16.88	15.80	16.81	16.81	14.96	15.11	17.31	17.25
<b>Na<sub>2</sub>O</b>	0.26	0.09	0.00	0.28	0.82	0.41	0.58	0.69
<b>K<sub>2</sub>O</b>	10.06	9.95	9.65	9.75	8.79	8.47	9.45	9.39
<b>Total</b>	96.59	96.50	97.05	96.74	97.24	95.99	97.39	96.72
<b>Si</b>	5.35	5.47	5.49	5.36	5.45	5.43	5.43	5.44
<b>Al<sup>(4)</sup></b>	2.65	2.53	2.51	2.64	2.55	2.57	2.57	2.56
<b>Al<sup>(6)</sup></b>	0.40	0.40	0.40	0.30	2.36	0.54	0.44	0.36
<b>Ti</b>	0.44	0.52	0.40	0.40	0.33	0.28	0.29	0.33
<b>Cr</b>	0.00	0.00	0.00	0.09	0.03	0.00	0.04	0.07
<b>Fe</b>	1.25	1.29	1.41	1.39	1.83	1.72	1.34	1.31
<b>Mg</b>	3.63	3.40	3.48	3.63	3.25	3.29	3.69	3.71
<b>Na</b>	0.07	0.02	0.00	0.08	0.23	0.12	0.16	0.19
<b>K</b>	1.93	1.83	1.78	1.80	1.63	1.58	1.73	1.73
<b>Total</b>	15.72	15.47	15.47	15.69	15.66	15.53	15.69	15.70

**Table 3: Representative orthoamphibole compositions, calculated to 23 oxygen. The Fe<sup>3+</sup> contents were determined using equation 5 of Droop (1987). DV3 is from the isograd, I7 and K7b are from the hydrated zone**

wt %	Gedrite			Anthophyllite		
	DV3	I7	Kb	DV3	I7	K7b
<b>SiO<sub>2</sub></b>	42.45	38.10	38.87	54.19	51.11	48.6
<b>TiO<sub>2</sub></b>	0.04	0.00	0.00	0.02	0.00	0.00
<b>Al<sub>2</sub>O<sub>3</sub></b>	20.68	15.10	15.27	2.47	3.00	1.14
<b>Cr<sub>2</sub>O<sub>3</sub></b>	0.00	0.00	0.00	0.20	0.25	0.23
<b>Fe<sub>2</sub>O<sub>3</sub></b>	0.00	11.71	11.18	1.69	7.01	11.74
<b>FeO</b>	16.53	18.65	17.06	16.63	14.71	19.11
<b>MnO</b>	0.10	0.29	0.20	0.09	0.00	0.29
<b>MgO</b>	15.19	13.09	13.91	22.27	21.92	17.19
<b>CaO</b>	0.14	0.23	0.17	0.16	0.00	0.15
<b>Na<sub>2</sub>O</b>	2.27	1.50	1.59	0.17	0.00	0.00
<b>Total</b>	97.43	98.67	98.25	97.89	98.00	98.45
<b>Si</b>	6.09	5.70	5.79	7.67	7.30	7.22
<b>Ti</b>	0.01	0.00	0.02	0.00	0.00	0.00
<b>Al</b>	3.49	2.66	2.68	0.42	0.51	0.20
<b>Cr</b>	0.00	0.00	0.00	0.02	0.03	0.03
<b>Fe<sup>3+</sup></b>	0.00	1.31	1.25	0.18	0.75	1.31
<b>Fe<sup>2+</sup></b>	1.98	2.32	2.12	1.97	1.75	2.37
<b>Mn</b>	0.01	0.04	0.03	0.02	0.00	0.04
<b>Mg</b>	3.25	2.92	3.08	4.70	4.66	3.81
<b>Ca</b>	0.04	0.04	0.03	0.02	0.00	0.02
<b>Na</b>	0.63	0.45	0.47	0.05	0.00	0.00
<b>Total</b>	15.50	15.44	15.47	15.05	15.00	15.00

**Table 4: Representative garnet compositions; the mineral formulae were calculated to 24 oxygen. Granulite zone analyses are rim compositions. Isograd and hydrated zone analyses are from second generation garnet overgrowths**

wt %	Granulite zone			At the isograd			Hydrated zone	
	C8d	C3a	H6	DV3	F19	D22	I7	K7b
<b>SiO<sub>2</sub></b>	39.60	40.66	39.37	40.06	38.63	38.32	38.41	38.98
<b>Al<sub>2</sub>O<sub>3</sub></b>	22.77	22.92	22.11	22.28	21.79	21.87	21.77	21.74
<b>Cr<sub>2</sub>O<sub>3</sub></b>	0.19	0.13	0.00	0.14	0.00	0.26	0.00	0.00
<b>FeO</b>	25.57	24.83	27.81	29.77	32.08	31.66	30.57	30.69
<b>MnO</b>	0.75	0.70	0.53	0.56	0.74	0.29	0.53	0.48
<b>MgO</b>	9.75	10.22	10.60	7.31	7.48	7.81	7.81	7.78
<b>CaO</b>	1.47	1.93	0.59	1.31	1.17	1.04	1.64	1.42
<b>Total</b>	100.10	101.39	101.01	101.39	101.88	101.25	100.73	101.09
<b>Si</b>	6.02	6.02	5.97	6.11	5.95	5.92	5.94	5.99
<b>Al</b>	4.08	4.10	3.95	4.01	3.95	3.98	3.97	3.94
<b>Cr</b>	0.02	0.01	0.00	0.02	0.00	0.03	0.00	0.00
<b>Fe</b>	3.25	3.10	3.53	3.80	4.13	4.09	3.95	3.95
<b>Mn</b>	0.10	0.09	0.07	0.07	0.10	0.04	0.07	0.06
<b>Mg</b>	2.21	2.27	2.39	1.66	1.72	1.79	1.80	1.78
<b>Ca</b>	0.24	0.31	0.10	0.21	0.19	0.17	0.27	0.23
<b>Total</b>	15.92	15.90	16.01	15.88	16.04	16.02	16.00	15.95

**Table 5: Representative cordierite and orthopyroxene compositions. Cordierite formulae were calculated to 18 oxygen, orthopyroxene formulae were calculated to 6 oxygen. Samples C3a and C8d are from the granulite zone, DV3 is from the isograd and I7 is from the zone of hydration**

wt %	Cordierite		Orthopyroxene			
	C3a	DV3	C8d	C3a	DV3	I7
<b>SiO<sub>2</sub></b>	50.01	48.76	51.18	50.89	51.12	52.96
<b>Al<sub>2</sub>O<sub>3</sub></b>	33.36	32.81	5.60	6.27	2.87	2.99
<b>Cr<sub>2</sub>O<sub>3</sub></b>	0.00	0.00	0.34	0.22	0.28	0.00
<b>FeO</b>	2.62	3.83	20.02	20.53	23.61	23.34
<b>MnO</b>	0.00	0.00	0.15	0.16	0.21	0.00
<b>MgO</b>	11.95	10.73	22.52	21.78	22.15	22.06
<b>CaO</b>	0.00	0.00	0.10	0.01	0.08	0.00
<b>Na<sub>2</sub>O</b>	0.06	0.10	0.00	0.00	0.00	0.00
<b>Total</b>	98.00	96.25	99.91	99.86	100.32	101.35
<b>Si</b>	5.03	5.02	1.88	1.87	1.91	1.93
<b>Al</b>	3.95	3.98	0.24	0.27	0.13	0.13
<b>Cr</b>	0.00	0.00	0.01	0.01	0.01	0.00
<b>Fe</b>	0.22	0.33	0.62	0.63	0.74	0.71
<b>Mn</b>	0.00	0.00	0.00	0.00	0.01	0.00
<b>Mg</b>	1.79	1.65	1.23	1.19	1.20	1.20
<b>Ca</b>	0.00	0.00	0.01	0.00	0.00	0.00
<b>Na</b>	0.01	0.02	0.00	0.00	0.00	0.00
<b>Total</b>	11.00	11.00	3.99	3.97	4.00	3.97

## LEUCOSOME COMPOSITIONS IN THE SMZ

In this section, leucosome compositions from both zones are compared to those of glasses produced in a series of fluid-absent biotite melting experiments investigating the influence of bulk rock chemical characteristics on the anatexis of metasedimentary protoliths (Stevens, 1995). These glass compositions are useful as they probably very closely replicate the initial melt compositions produced by biotite fluid-absent melting in the SMZ. In this terrane, biotite was never exhausted, and the natural melts coexisted with garnet and sillimanite, garnet and orthopyroxene, or orthopyroxene and cordierite (Stevens and Van Reenen, 1992a), as they did in the run products from experiments on comparable bulk compositions. Representative leucosome compositions from both the hydrated and granulite zones, and the experimentally produced glass compositions are listed in Table 6 (details of the starting compositions, experimental procedures, results, and analytical techniques are given in Stevens *et al.* (1995)).

Prior to a comparison of the glass and leucosome compositions, it should be considered that the leucosomes represent mixtures with unknown ratios of melt and residual crystals. On the other hand, the experimental glass compositions represent pure melts that had no chance to re-equilibrate with the residual assemblage on cooling. In the natural rocks, it is likely that, due to the slow cooling rates of regional metamorphism, the melts will have re-equilibrated, to some degree, with the residual assemblage in the host rocks. This problem will be most acute in the case of narrow leucosome veins, where none of the melt is far removed from the adjacent granulite-grade assemblage. Fractional crystallisation and melt loss after partial crystallisation can also significantly alter leucosome compositions from those of the initial melts.

The SMZ leucosome compositions clearly differ from the proposed compositions of the initial melts (experimental glasses). There are also distinct differences between the granulite zone leucosomes and the hydrated-zone leucosomes. All of the natural leucosomes have substantially lower  $K_2O$  contents than the glasses. This is reflected by the ratio of normative orthoclase relative to total normative feldspar content ( $Or'$ ). The leucosomes in the granulite-zone are generally less  $K_2O$ -rich than those in the hydrated zone. Normative plagioclase compositions ( $Ab'$ ) are significantly more calcic in the granulite-zone leucosomes than in either the hydrated-zone leucosomes or the glasses. The hydrated-zone leucosomes have normative plagioclase compositions that are similar to, but slightly more albitic than those of the glasses. The leucosomes generally have lower total  $FeO + MgO$  than the glasses.  $Mg\#s$  in the hydrated-zone leucosomes are generally similar, or lower than those in the glasses. Leucosome  $Mg\#s$  in the granulite zone are generally higher than those in the glasses.

### Conclusions Based on the Compositions of the Leucosomes

The above comparison suggests that granulite-zone leucosomes represent crystal cumulates of quartz and plagioclase (Fig. 10) and that this portion of the SMZ has lost an appreciable quantity of melt. Even the most potassic, lowest  $Mg\#$  leucosomes in the granulite zone have normative plagioclase compositions that are significantly more calcic than those of the glasses. This cannot be the result of a substantially higher degree of melting in the natural rocks than in the experimental charges, since neither biotite, quartz nor plagioclase was exhausted by the melting reactions in the SMZ. Melt fractions and melt compositions thus remained buffered by the same biotite-quartz-plagioclase consuming equilibria as in the experiments.

In the case of the hydrated-zone leucosomes, normative plagioclase compositions are slightly more albitic than those in the glass. This might be a function of slightly lower degrees of melting than represented by the glass compositions. Alternatively, the starting plagioclase

**Table 6: (a) Representative leucosome compositions from the granulite zone of the SMZ.(b) Representative leucosome compositions from the hydrated-zone of the SMZ, as well as some experimental glass compositions. M1 - 875 °C, 0.5 GPa; M2 - 850 °C, 1 GPa. A1 - leucosomes coexisting with garnet and sillimanite, A2 - leucosomes coexisting with garnet and orthopyroxene, A3 - leucosomes coexisting with cordierite and orthopyroxene. The wt% totals have been normalised to 100%. Ab' = (100.Ab/Ab + An), Or' = (100.Or/Or + Ab + An)**

**(a)**

wt%	A 1					A 2		A 3
	C 5	A 13	G 5	C 10	B 6	C 12	B 9	C 25
SiO <sub>2</sub>	72.49	75.38	75.02	75.30	76.94	76.25	79.93	75.47
TiO <sub>2</sub>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.08
Al <sub>2</sub> O <sub>3</sub>	17.57	16.49	15.98	15.92	14.37	14.79	13.27	15.44
Fe <sub>2</sub> O <sub>3</sub>	0.00	0.13	0.05	0.33	0.06	0.00	0.09	0.00
FeO	0.43	0.15	0.15	0.59	0.19	0.66	0.18	1.01
MnO	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
MgO	0.36	0.09	0.09	0.16	0.14	0.61	0.31	1.94
CaO	3.52	2.48	3.28	1.26	2.33	3.36	2.48	2.48
Na <sub>2</sub> O	4.32	4.07	3.82	4.04	4.20	3.77	3.00	2.73
K <sub>2</sub> O	1.31	1.21	1.61	2.40	1.77	0.57	0.84	0.85
Q	33.91	41.55	39.37	39.31	40.40	43.48	53.75	47.34
C	2.65	3.98	1.98	4.39	1.30	1.86	3.02	5.52
Or	7.74	7.15	9.51	6.25	10.46	3.37	4.37	5.02
Ab	36.56	34.44	32.32	34.19	35.54	31.90	25.39	23.10
An	17.46	12.30	16.27	14.18	11.56	16.67	12.30	12.3
Opx	1.69	0.39	0.46	1.21	0.65	2.73	1.03	6.56
Mt	0.00	0.19	0.07	0.48	0.9	0.00	0.13	0.00
IIm	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.15
Mg#	60	56	47	33	53	62	75	77
Ab'	67.67	73.68	65.51	70.68	75.46	65.67	65.25	65.25
Or'	12.53	13.26	16.36	11.44	18.17	6.48	12.42	12.42

**(b)**

	A 1				A 2		Glasses	
	K 9	N 12	O 5a	P 8	E 11	K 13	M 1	M 2
SiO <sub>2</sub>	74.35	75.84	73.75	74.44	74.69	74.87	73.57	73.47
TiO <sub>2</sub>	0.04	bd	0.03	0.06	0.14	0.09	0.24	0.29
Al <sub>2</sub> O <sub>3</sub>	15.68	15.18	16.10	15.81	15.64	15.74	14.44	14.58
Fe <sub>2</sub> O <sub>3</sub>	na	na						
FeO	0.97	1.06	0.61	0.75	0.64	0.77	1.74	1.69
MnO	0.07	0.08	0.09	0.03	0.08	0.05	0.00	0.00
MgO	0.12	0.14	0.18	0.28	0.05	0.19	0.45	0.51
CaO	1.47	1.54	1.12	1.00	1.58	1.73	0.99	0.96
Na <sub>2</sub> O	4.21	4.82	4.94	3.87	4.70	4.25	3.67	3.83
K <sub>2</sub> O	3.09	1.28	3.29	3.76	2.39	2.31	4.90	4.67
Q	33.86	38.71	29.19	34.37	34.47	36.80	29.40	39.30
C	2.73	3.07	2.38	3.55	2.45	2.83	1.29	1.47
Or	18.26	7.56	19.44	22.22	14.12	13.69	28.95	27.60
Ab	35.62	40.79	41.80	32.74	39.77	36.06	31.03	32.41
An	7.29	7.64	5.56	4.96	7.84	8.61	4.91	4.76
Opx	2.14	2.44	1.69	2.03	1.22	1.83	3.92	3.89
Mt	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
IIm	0.08	0.00	0.06	0.11	0.27	0.17	0.46	0.56
Mg#	14	19	45	34	12	26	32	32
Ab'	83.01	84.20	88.26	86.84	83.53	80.73	81.63	81.36
Or'	29.85	13.50	29.10	37.08	22.87	23.46	51.99	56.13

composition in the natural rocks might have been more sodic than that used in the experiments. However, this difference could not have been large as the plagioclase used in the reported experiments was more albite than that in the granulite-zone metapelites. Based on the normative plagioclase compositions, and the normative Q:Ab ratios (Fig. 10), it appears that the hydrated-zone leucosomes have lost a smaller quantity of melt than those of the granulite zone. However, the K<sub>2</sub>O contents of these leucosomes are generally low compared to the glasses. In both zones, orthopyroxene and cordierite crystals of the leucosomes and in the associated metapelites, are consumed by reactions producing biotite where melt is inferred as a reactant. These ferromagnesian phases are rare in the leucosomes but are abundant in the host metapelites. It is proposed that K<sub>2</sub>O transfer from the leucosomes to the host rocks has been effective in altering the leucosome K<sub>2</sub>O concentrations, particularly in the case of small *in-situ* veins.

In summary, the leucosome compositions have been substantially altered through fractional crystallisation, melt-loss, and back-reaction with the host metasediments. It is concluded, largely on the basis of the normative plagioclase compositions, and normative Q, Ab and Or proportions, that the granulite zone has lost substantially more melt than the hydrated zone. In consequence, the hydrated-zone leucosomes remained more hydrous and more potassic than those in the granulite zone.

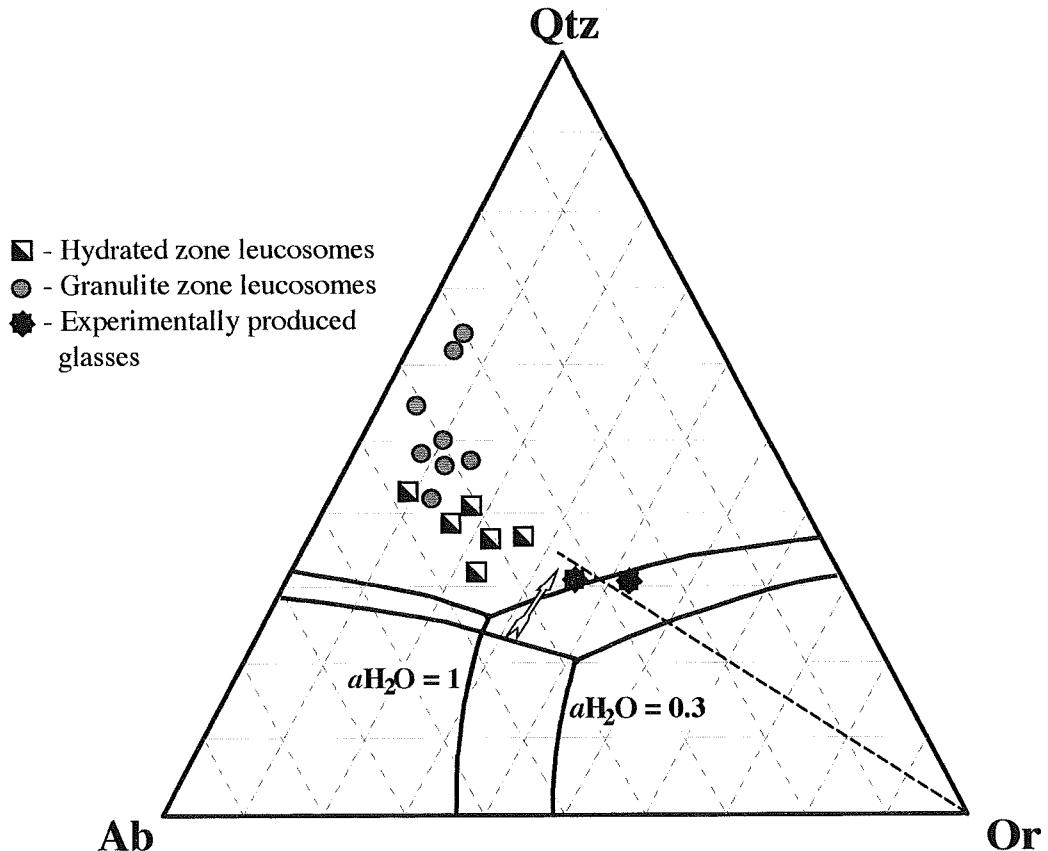


Figure 10: A plot of normative Q, Ab and Or in the SMZ leucosomes and the glass compositions listed in Table 6 on the haplogranite phase diagram at 1 GPa of Ebadi and Johannes (1991). The granulite zone leucosomes have the composition of cumulates of quartz and plagioclase. Those of the hydrated zone are also K<sub>2</sub>O-poor, but extrapolate along a line of K-feldspar enrichment close to the glass compositions. The arrow indicates the direction of the evolution of the eutectic with decreasing pressure.

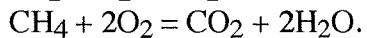
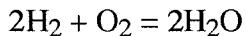
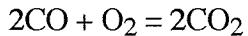
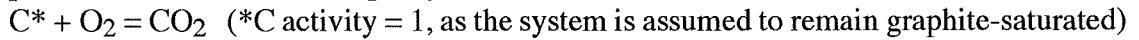
## P-T-X<sub>FL</sub> CONDITIONS OF HYDRATION

The garnet-biotite thermometry published by Van Reenen (1986) suggested that in the retrogressed zone the final equilibration temperature was  $\sim 600$  °C. The presence of kyanite in these rocks suggests a minimum pressure of 0.6 GPa at this time. Temperatures calculated in this study using the garnet-biotite geothermometer of Ferry and Speer (1978), and the mineral compositions in Tables 2 and 4, indicate temperatures of between 580 and 600 °C for reaction (v) in the hydrated zone. The temperature of occurrence of this reaction in the granulite zone is difficult to establish. The degree of reaction in this zone is very small and although garnet compositions can be obtained, it is impossible to identify a discrete the biotite composition produced by the reaction. Similar problems exist in trying to establish the temperature of occurrence of reactions (i) and (ii) that also produce biotite. These reactions have not produced garnet and it is thus not possible to be certain that the biotite resulting from the crystallisation-hydration reactions has equilibrated with the rims of the poikilitic granulite-grade garnets. Pairing the reaction (i) biotite and the high-grade garnet rim compositions produces temperatures that range between  $\sim 700$  and  $\sim 670$  °C. Due to the uncertainties about garnet equilibration these should be regarded as maximum estimates.

The mineral textures produced in the reactions that are inferred to have involved a fluid all have an association with graphite, indicating that CO<sub>2</sub> was a component of the fluid. This could not have been evolved from the melts, as the solubility of CO<sub>2</sub> in granite at 0.6 GPa is negligibly small (Holloway, 1976). The metasediments in both zones, however, contain a graphite component, interpreted to represent original biogenic graphite (Venneman and Smith, 1992). It is useful, at this point, to consider the interaction between melt-derived pure H<sub>2</sub>O and this graphite.

### Graphite Oxidation

To derive fluid compositions at the time of melt H<sub>2</sub>O saturation it is necessary to consider possible reactions in the simple system C-O-H, i.e.;



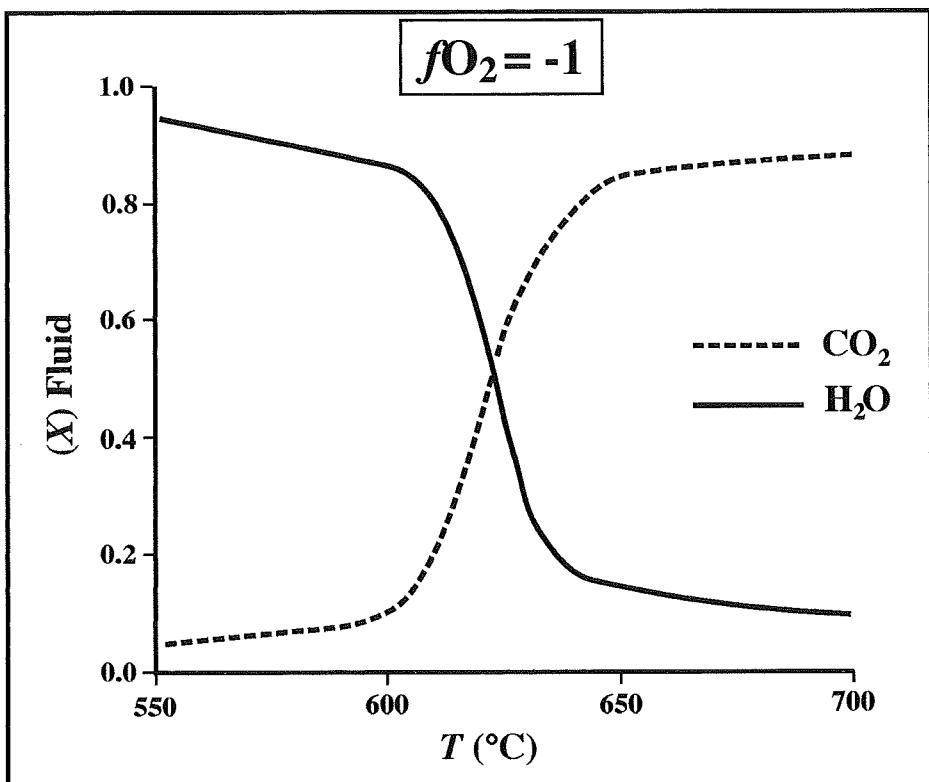
Equilibrium fluid compositions were calculated using the modified Redlich Kwong equation of state plus the equations for log K of Ohmoto and Kerrick (1977). The calculations assume ideal mixing of fluid species, graphite saturation and  $fO_2$  buffered at the quartz-fayalite-magnetite buffer(QFM), one log unit below QFM, and two log units below QFM. Calculated fluid compositions in equilibrium with graphite at 0.6 GPa and between 600 to 700 °C are listed in Table 7.

Irrespective of the chosen  $fO_2$  conditions, there is a sharp change in calculated fluid composition between 650 and 600 °C, fluids at lower temperature become progressively more H<sub>2</sub>O-rich (Fig. 11). H<sub>2</sub>O and CO<sub>2</sub> are the only significant volatile species in the fluid. Assuming  $fO_2$  to be buffered at QFM -1 the composition of the fluid would change from XH<sub>2</sub>O = 0.14 at 650 °C, to XH<sub>2</sub>O = 0.87 at 600 °C.

In the natural rocks, fluid-present conditions would have been attained at the moment that the melts became H<sub>2</sub>O-saturated. The relatively oxidising H<sub>2</sub>O-rich fluid would have reacted with graphite, evolving towards an equilibrium fluid composition. The final fluid composition, and the fluid volume, would have depended on the equilibrium fluid composition and the relative amounts of H<sub>2</sub>O and graphite in the system. If insufficient graphite were available to attain the graphite buffered equilibrium composition, a less voluminous, more H<sub>2</sub>O-rich fluid,

**Table 7: Calculated fluid compositions in equilibrium with graphite at 0.6 GPa**

		600 °C	650 °C	700 °C
Q	$X\text{CO}_2$	0.265	0.946	0.962
	$X\text{H}_2\text{O}$	0.727	0.051	0.034
	$X\text{CH}_4$	0.000	0.000	0.000
	$X\text{CO}$	0.000	0.003	0.004
	$X\text{H}_2$	0.008	0.001	0.001
F	$X\text{CO}_2$	0.100	0.844	0.885
	$X\text{H}_2\text{O}$	0.871	0.142	0.098
	$X\text{CH}_4$	0.000	0.000	0.000
	$X\text{CO}$	0.001	0.008	0.012
	$X\text{H}_2$	0.028	0.006	0.005
M	$X\text{CO}_2$	0.032	0.611	0.687
	$X\text{H}_2\text{O}$	0.878	0.326	0.241
	$X\text{CH}_4$	0.001	0.001	0.001
	$X\text{CO}$	0.001	0.018	0.029
	$X\text{H}_2$	0.088	0.044	0.042
-1	$X\text{CO}_2$	0.100	0.844	0.885
	$X\text{H}_2\text{O}$	0.871	0.142	0.098
	$X\text{CH}_4$	0.000	0.000	0.000
	$X\text{CO}$	0.001	0.008	0.012
	$X\text{H}_2$	0.028	0.006	0.005
-2	$X\text{CO}_2$	0.032	0.611	0.687
	$X\text{H}_2\text{O}$	0.878	0.326	0.241
	$X\text{CH}_4$	0.001	0.001	0.001
	$X\text{CO}$	0.001	0.018	0.029
	$X\text{H}_2$	0.088	0.044	0.042



*Figure 11: Calculated fluid compositions expressed as a function of  $\text{XH}_2\text{O}$ ,  $\text{XCO}_2$  and  $T$ .  $P=0.6 \text{ GPa}$  and  $f\text{O}_2$  was assumed to be buffered one log unit below QFM. See text for the calculation method.*

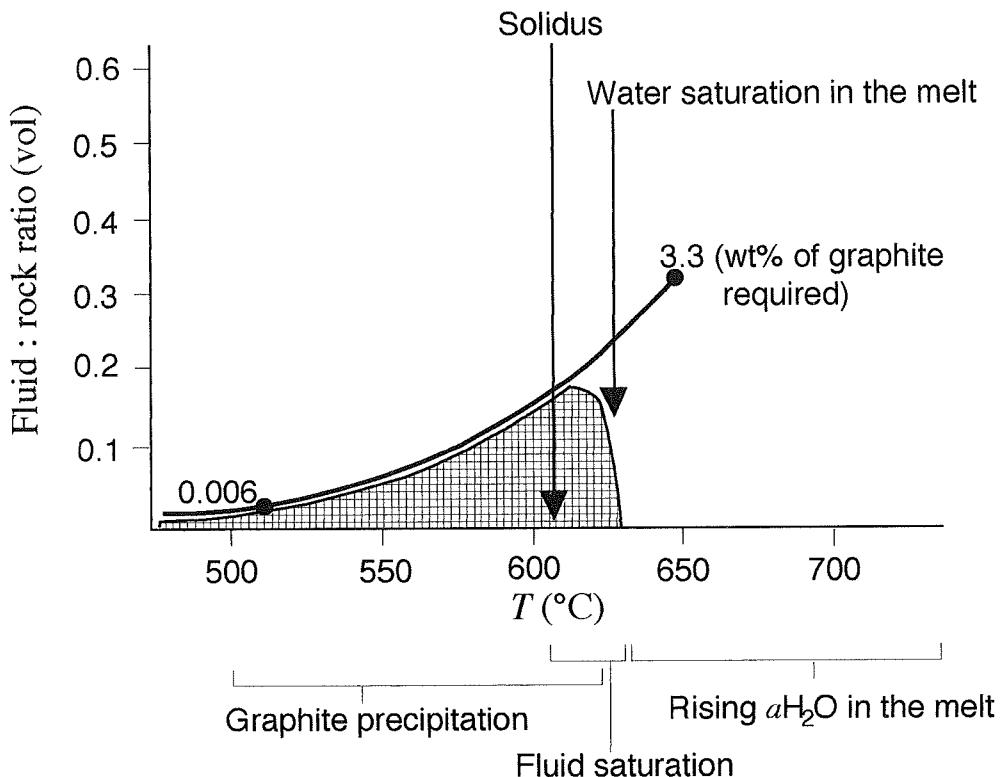
not coexisting with graphite, would result. If the amount of  $H_2O$  in the rock, the equilibrium fluid composition, and the molar volumes of the equilibrium fluids at  $P$  and  $T$  are known, then the amount of graphite that would be required, and the resultant fluid:rock ratio, can be calculated. To do this it is necessary to deal with a representative volume of migmatite and treat it as a homogeneous unit. Field observations suggest that 25% partial melt is a realistic estimate for the SMZ metapelites at peak  $P$ - $T$  conditions (Stevens, 1992). Biotite-melt coexistence during fluid-absent biotite melting buffers the melt  $H_2O$  content to values very close to 3 wt% for all pressures between 0.5 and 1 GPa (Vielzeuf and Montel, 1994). Molar volumes of the mixed fluids at 0.6 GPa and between 500 and 700 °C were calculated by means of MRKZ, a program written by J.D. Clemens to calculate molar volumes of fluid species and mixtures using the modified Redlich Kwong equation of state as given by Holloway (1981). Thus, it can be calculated that, at 650 °C and 0.6 GPa, if all the  $H_2O$  formerly residing in the melt were available for reaction, the fluid:rock ratio would be > 30 vol %, if an equilibrium fluid composition were produced (Fig. 12). This substantial fluid volume is a function of both the  $CO_2$ -dominated nature of the fluid (a little  $H_2O$  produces a lot of  $CO_2$ -dominated fluid) and the relatively high molar volume of such a  $CO_2$ -rich fluid. It would, however, require that the rocks have at least 3.3 wt% graphite prior to crystallisation (Fig 12). In the SMZ the solidus was probably intersected close to 620 °C. This would have resulted in less voluminous, less  $CO_2$ -rich fluids that would have required less graphite to produce. However, from Figure 13 it can be seen that fluid:rock ratios as high as 1:5, by volume, are likely for SMZ rocks where graphite was sufficiently abundant.

Falling temperature, and the retrograde hydration reactions documented in the previous section, would have resulted in graphite precipitation. This is confirmed by the textures. As original carbon isotopic heterogeneities are preserved in the SMZ, either a substantial amount of graphite remained unreacted, or graphite oxidation, subsequent hydration reactions, and resultant graphite precipitation all occurred essentially *in situ*, with little or no fluid mixing.

Reaction (v) is extensively developed in the hydrated zone and must involve a  $K_2O$ -bearing phase. None of the metasediments contains K-feldspar, and melt is assumed to have been the only  $K_2O$ -rich phase other than biotite. It was concluded, on the basis of a textural association with graphite, that the reaction occurred in a fluid-present environment. Thus, it appears that the fluid-present hydration reactions occurred in the narrow temperature interval of melt-fluid coexistence, as also suggested by the geothermometry. Under these circumstances, the reactions appears to be a powerful mechanism for depleting the leucosomes in  $K_2O$ .

## CONCLUSIONS

The findings of this study appear to resolve a long-standing inconsistency between the stable isotopic and mineralogical characteristics of the SMZ hydrated rocks. The rocks *did* interact with an extensive, pervasive,  $H_2O$ -undersaturated fluid, but it was internally derived and thus, the isotope systematics carry no record of fluid infiltration. The petrographic investigation of the hydration reactions illustrates the degree to which fluid availability has controlled the retrogression. In many of the rocks, disequilibrium assemblages are preserved simply because there was insufficient fluid with which to react. Melt migration out of the granulite zone, probably at conditions approaching the peak of metamorphism, was more effective than in the hydrated zone. Consequently, in the hydrated zone much of the  $H_2O$ , partitioned into the leucosomes during prograde melting, was released back into the rocks during cooling. This occurred through reactions between melt and high-grade phases and reactions between fluid and high-grade phases in the presence of a melt. In the hydrated zone  $H_2O$  was effectively recycled between fluid-absent melting equilibria on the prograde path and crystallisation hydration equilibria on the retrograde path.



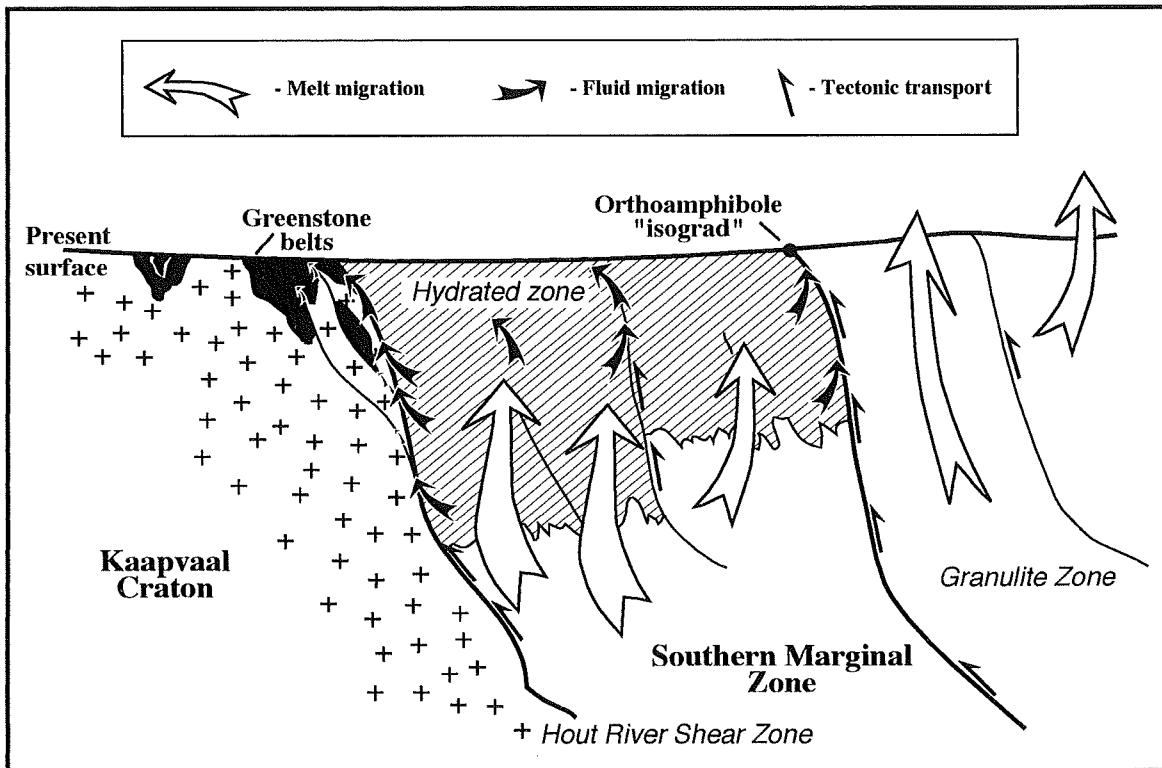
*Figure 12: Calculated fluid:rock ratios (heavy curve) generated if the equilibrium fluid composition was attained. The calculations assume a 25 % partially melted migmatite with 3 wt%  $H_2O$  in the melt and graphite saturation. Fluid compositions used are those in Figure 12. Mixed fluid molar volumes were calculated by means of MRKZ, a program written by J.D. Clemens. The points on the heavy line indicate the quantity of graphite required in the rock to ensure graphite saturation at 520 and 650 °C. The hatched area represents the likely fluid:rock ratios attained in the SMZ.*

The orthoamphibole used to delineate the retrograde isograd appears to be a transitory reaction product that is overprinted by the same biotite-garnet-producing reaction in both the granulite zone and the hydrated zone. It can therefore have no grade-related relevance for the end of the retrogression period. The consumption of orthoamphibole by reaction (v) appears to be driven by an increase in the size of the equilibration volume in the rocks as the fluid phase became abundant, and possibly also by an increase in  $aK_2O$  in the fluid as  $XCO_2$  declined through falling  $T$ . However, kinetic factors may also be important. Garnet is observed to always nucleate on old garnet cores. Thus, in rocks containing little garnet after the M2 decompression period, kinetic factors may have favoured the initial production of orthoamphibole, which is then overprinted by the final garnet-biotite assemblage.

The pervasive nature of the hydration event in the SMZ is probably the result of the large fluid phase volume increases brought about by the production of  $CO_2$  through graphite oxidation. In a general context, high-grade reactions that produce  $H_2O$  in graphitic rocks appear to be an unconsidered source of low  $aH_2O$  fluids in the crust.

In this study it is concluded that the previously proposed orthoamphibole retrograde "isograd" does not represent a reaction front resulting from a change in grade ( $P-T$ ); rather it seems most likely to be a fault boundary between two high-grade SMZ blocks with different  $H_2O$  contents, due to different degrees of melt loss (Fig. 13). This is possibly reflected in the

fact that the highest temperature A3 leucosome forming reaction,  $Bt + Qtz + Pl = Crd + Opx + Melt$ , has not been identified from the hydrated zone, indicating slightly lower maximum temperatures of equilibration than in the granulite zone. In addition to this, rocks from the granulite zone with  $Mg\# < 65$  never contain cordierite (Van Reenen, 1983). However, in this study many hydrated zone samples with  $Mg\#s < 60$  were found to contain cordierite. This must reflect a lower pressure of equilibration at the end of the M2 decompression event in this zone. These metamorphic data are consistent with the hydrated zone representing a slightly shallower, slightly cooler crustal level than the granulite zone during the peak of metamorphism. The data presented in this study do not preclude the addition of some melt to the hydrated zone from a deeper level metasedimentary source that probably retains granulite grade assemblages (Fig. 13).



*Figure 13: An interpretation of the relationship between the Kaapvaal Craton and the two zones of the SMZ, as suggested by the data presented in this study. In this scenario the orthoamphibole isograd is a fault boundary and is not grade related. Escaping hydrated zone fluids may have blurred this relationship slightly by interacting to a minor degree with the overlying granulite zone. This would depend on syn-retrogression thrusting. Open arrows indicate melt migration, filled arrows indicate fluid migration.*

## SUGGESTIONS FOR FUTURE WORK

Previous metamorphic studies have emphasised the influx of externally derived fluids into the SMZ. This model has been extended to also account for the fluids producing gold mineralisation in uplift related shear zones in the SMZ, and in related structures in greenstones near the SMZ-Kaapvaal Craton contact. As the fluid infiltration model does not appear valid for the retrogression of the bulk of the terrane, it would seem pertinent to investigate the mineralising potential of the in-situ derived fluids proposed in this study. The uplift-related deformation zones could well have been conduits for externally derived fluids. However, the mineralised areas are characterised by a similar biotite-garnet association as marks the end of the retrogression period in the former granulites. Thus, the mineralising fluids must have been migrating through the shear zones at close to the time when the fluids evolved from within the terrane would have been escaping from their sources. This may only be coincidence. Alternatively there may be a genetic relationship that warrants investigation, as a correct understanding of the origin of the mineralising fluid would certainly aid in locating potential sites of mineralisation.

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