

# The influence of cordierite on melting and mineral-melt equilibria in ultra-high-temperature metamorphism

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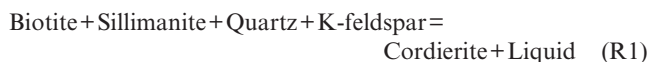
**ABSTRACT:** Experimentally constrained calibrations of the incorporation of H<sub>2</sub>O and CO<sub>2</sub> into cordierite as functions of P–T–*a*<sub>H<sub>2</sub>O</sub>–*a*<sub>CO<sub>2</sub></sub> are integrated with KFMASH grids which define mineral-melt equilibria in pelites. This is used to explore the impact of the volatile content and composition of cordierite on anatexis and melt-related processes in high-temperature (HT) and ultra-high-temperature (UHT) metamorphism. The strongly temperature-sensitive H<sub>2</sub>O content of cordierite coexisting with dehydration melts (0.4–1.6 wt.%) causes a 10–25% relative decrease in the amount of melt produced from pelites compared with models which treat cordierite as anhydrous.

KFMASH melting grids quantified for *a*<sub>H<sub>2</sub>O</sub> demonstrate consistency between the measured H<sub>2</sub>O contents in cordierite from granulite-migmatite terrains and mineral equilibria. These indicate anatexis with *a*<sub>H<sub>2</sub>O</sub> in the range 0.26–0.16 at 6–8 kbar and 870–930°C. The pressure-stability of cordierite+garnet with respect to orthopyroxene+sillimanite+quartz in KFMASH is strongly influenced by cordierite H<sub>2</sub>O content, which decreases from 1.1 to 0.5 wt.% along the melting reaction Grt+Crd<sub>H</sub>+Kfs=Opx+Sil+Qz+L. The lower-T invariant point involving biotite (8.8 kbar/900°C) that terminates this reaction has *a*<sub>H<sub>2</sub>O</sub> of 0.16 ± 0.03, whereas the higher-T terminating invariant point involving osumilite (7.9 kbar/940°C) occurs at *a*<sub>H<sub>2</sub>O</sub> 0.08 ± 0.02. Osumilite-bearing assemblages in UHT terrains imply *a*<sub>H<sub>2</sub>O</sub> of <0.08, and at 950–1000°C and 8–9 kbar calculated *a*<sub>H<sub>2</sub>O</sub> is only 0.04–0.02. Cordierites stable in osumilite-bearing assemblages or with sapphirine+quartz have maximum predicted H<sub>2</sub>O contents of ca. 0.2 wt.%, consistent with H<sub>2</sub>O measured in cordierites from two sapphirine-bearing UHT samples from the Napier Complex.

The addition of CO<sub>2</sub> to the H<sub>2</sub>O-undersaturated (dehydration-melting) system marginally decreases the temperature of melting because of the stabilisation of cordierite, the solid product of the peritectic melting reactions. The preferential incorporation of CO<sub>2</sub> enhances the stability of cordierite, even at fixed *a*<sub>H<sub>2</sub>O</sub>, and causes the stability fields of Grt+Crd+Sil+Kfs+Qz+L and Grt+Opx+Crd+Kfs+Qz+L to expand to higher pressure, and to both higher and lower temperatures. The minimum solubility of H<sub>2</sub>O in granitic melt is independent of the CO<sub>2</sub> content of cordierite, and the distribution of H<sub>2</sub>O between melt and cordierite is similar at a given melt H<sub>2</sub>O-content to the H<sub>2</sub>O-only system. This enhanced stability of CO<sub>2</sub>-bearing cordierite leads to a reduced stability range for osumilite-bearing assemblages to temperatures of ca. 950–975°C or greater. Cordierites in the Napier Complex UHT gneisses contain 0.5 and 1.05 wt.% CO<sub>2</sub>, consistent with a role for CO<sub>2</sub> in stabilising cordierite with respect to osumilite in these unusual sapphirine-bearing granulites.

**KEY WORDS:** Fluids, granites, granulites, osumilite, sapphirine.

The H<sub>2</sub>O-CO<sub>2</sub>-bearing phase cordierite (Schreyer 1985) is involved in many key mineral equilibria in high-temperature (HT) and ultra-high-temperature (UHT) metamorphism (Hensen 1971, 1986; Hensen & Green 1973; Aranovich & Podlesskii 1989; Vry *et al.* 1990; Bertrand *et al.* 1991; Harley 1998a). It is also central to many of the reactions controlling melting (Vielzeuf & Holloway 1988; Patiño Douce & Johnston 1991; Carrington & Harley 1995a; Stevens *et al.* 1995; Holland *et al.* 1996; Harley 1998a; White *et al.* 2001), being a modally and texturally significant phase in regional granulite terranes which exhibit migmatization, melt mobilisation and melt extraction (Waters 1988; Fitzsimons 1994, 1996; Harley 1994; Harley *et al.* 2002). From the viewpoint of peraluminous granite melt production in the middle crust, dehydration-melting of biotite-bearing mineral assemblages in pelites with moderate to high X<sub>Mg</sub> (>0.5) is often controlled by divariant, or higher variance, cordierite-forming reactions such as the model KFMASH (K<sub>2</sub>O-FeO-MgO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>-H<sub>2</sub>O) reaction:



producing cordierite migmatites and cordierite-bearing leucogranites at 2.5–7 kbar and 750–900°C (e.g. Waters 1988; Fitzsimons 1996; Kriegsman 2001). Hence, an understanding of the consequences of cordierite as a volatile-bearing phase that can take up H<sub>2</sub>O and CO<sub>2</sub> is critical to evaluation of melting processes and useful for the calculation of fluid activities potentially accompanying melt production. With respect to HT and UHT metamorphism, the stability of cordierite in both the presence and absence of melt generally defines the lower temperature (T) and pressure (P) limits of mineral assemblages such as sapphirine+quartz and orthopyroxene+sillimanite+quartz, which are critical to establishing the progress and conditions of UHT metamorphism. Therefore, an understanding of the stability limits of cordierite and their dependence on its H<sub>2</sub>O and CO<sub>2</sub> content is central to any evaluation of UHT metamorphism and



the role of melts and melt extraction in stabilising UHT assemblages (e.g. Harley 1998a; Kriegsman 2001; White & Powell 2002; Kelsey *et al.* 2003).

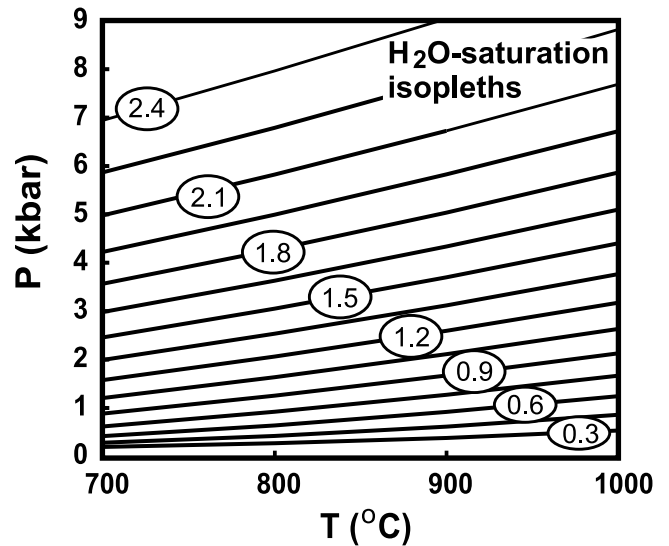
In the present contribution, the authors first overview and summarise the experimental constraints on the P–T– $a_{\text{H}_2\text{O}}$ – $a_{\text{CO}_2}$  dependencies on the uptake of H<sub>2</sub>O and CO<sub>2</sub> in cordierite, and the distribution of H<sub>2</sub>O between coexisting granitic melt and cordierite. They then go on to integrate this data with phase equilibrium experiments and calculations pertinent to HT/UHT melting and metamorphism in order to examine the impact of cordierite as a peritectic phase in migmatites, and the effect of CO<sub>2</sub> on melting and other phase relations. Finally, they also document and evaluate fluid activities calculated based on cordierite compositions from selected HT and UHT terrains.

## 1. Incorporation of H<sub>2</sub>O and CO<sub>2</sub> into cordierite under HT/UHT conditions

The importance of cordierite as a phase with variable H<sub>2</sub>O and CO<sub>2</sub> has long been recognised (Goldman *et al.* 1977; Newton & Wood 1979; Armbruster & Bloss 1982; Aines & Rossman 1984). This is expressed in its general formula (Mg, Fe)<sub>2</sub>Al<sub>4</sub>Si<sub>5</sub>O<sub>18</sub>.*n*H<sub>2</sub>O.*m*CO<sub>2</sub>, where ‘*n*’ and ‘*m*’ are the number of molecules of H<sub>2</sub>O and CO<sub>2</sub> respectively, per nine cations (18 oxygen volatile-free) formula unit. It should be noted that this formula is a simplification of the chemistry of cordierite, which also generally incorporates alkalis (Li, Na, K) and Be in its structure (Goldman *et al.* 1977; Armbruster & Bloss 1982; Schreyer 1985; Kalt, 2000). However, Na and K do not appear to exert a strong influence on the H<sub>2</sub>O and CO<sub>2</sub> uptake in cordierite compared with the effects of P–T and fluid composition (Thompson *et al.* 2002). The uptake of H<sub>2</sub>O and CO<sub>2</sub> by cordierite under fluid-present conditions has been assessed in several experimental studies which have generally involved equilibrating (or attempting to equilibrate) natural or synthetic cordierite with H<sub>2</sub>O, H<sub>2</sub>O–CO<sub>2</sub> or CO<sub>2</sub> fluids under P–T conditions in the range 1–9 kbar and 500–800°C (Mirwald *et al.* 1979; Kurepin 1985; Boberski & Schreyer 1990; LeBreton & Schreyer 1993; Carey 1995; Skippen & Gunter 1996).

Using a different approach to these earlier studies, Carrington & Harley (1996), Harley & Carrington (2001) and Thompson *et al.* (2001) equilibrated cordierite with peraluminous haplogranitic melt under both fluid-saturated and -undersaturated conditions, and in fluid-present experiments with pure H<sub>2</sub>O and with mixed H<sub>2</sub>O–CO<sub>2</sub> fluids. These experiments at P–T conditions of 3, 5 and 7 kbars and 800, 900 and 1000°C have enabled the formulation of new expressions relating the activity of H<sub>2</sub>O (Harley & Carrington 2001) and CO<sub>2</sub> (Harley *et al.* 2002) to the volatile contents of cordierite as measured by SIMS, and moreover, have defined the P–T– $a_{\text{H}_2\text{O}}$  dependence of the distribution of H<sub>2</sub>O between melt and cordierite,  $D_w$  (Harley & Carrington 2001). As with many of the earlier studies, and despite the spectroscopic evidence for distinct orientations for H<sub>2</sub>O in the cordierite channels (Armbruster & Bloss 1982; Schreyer 1985; Winkler *et al.* 1994), these experiments have demonstrated that a simple, one-site model adequately describes the incorporation of both H<sub>2</sub>O and CO<sub>2</sub> in P–T– $a_{\text{H}_2\text{O}}$ – $a_{\text{CO}_2}$  space. This one-site model defines the maximum total number of molecules of H<sub>2</sub>O (*n*) and CO<sub>2</sub> (*m*) potentially incorporated into cordierite to be unity (i.e.  $n+m=1$ ).

In the case of the incorporation of H<sub>2</sub>O into cordierite, the saturation H<sub>2</sub>O contents determined by Harley & Carrington (2001) are consistent with the majority of the previous lower-T experimental data in the cordierite–H<sub>2</sub>O system (Mirwald *et al.*



**Figure 1** Pressure–temperature diagram contoured with isopleths (isohydrons) of H<sub>2</sub>O in  $X_{\text{Mg}}=0.75$  cordierite coexisting with pure H<sub>2</sub>O fluid, as modelled by Harley & Carrington (2001). The isohydrons are expressed in terms of wt.% H<sub>2</sub>O.

1979; Boberski & Schreyer 1990; Mukhopadhyay & Holdaway 1994; Carey 1995; Skippen & Gunter 1996). Hence, Harley & Carrington (2001) combined their data with the previous work to obtain a P–T– $a_{\text{H}_2\text{O}}$  relationship for cordierite that is applicable over the T range 600–1000°C:

$$a_{\text{H}_2\text{O}} = [n/(1-n)] \cdot (\exp\{-4203(\pm 320)/T + 11.75(\pm 0.33)\}) / f_{\text{H}_2\text{O}}(P, T) \quad (1)$$

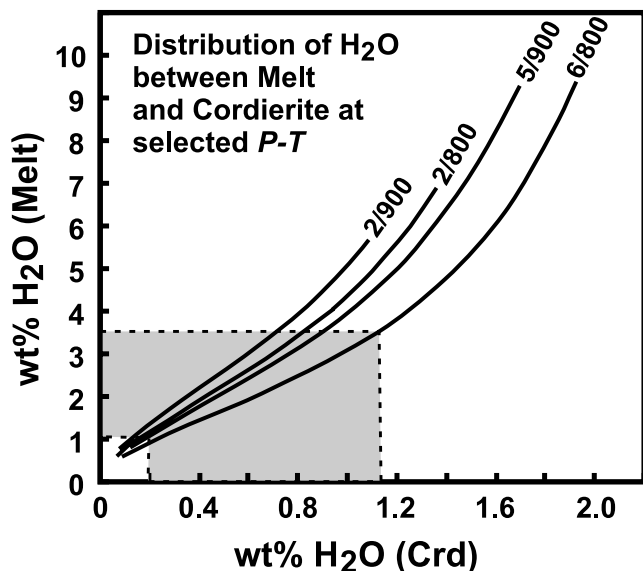
Setting  $a_{\text{H}_2\text{O}}=1$  and solving for ‘*n*’ at specified P, T and  $f_{\text{H}_2\text{O}}(P, T)$  produces the H<sub>2</sub>O isopleths (also known as isohydrons) presented in Figure 1. These isohydrons are within the error range of isopleths calculated from the thermodynamic data set of Holland & Powell (1998).

Of significance for melting relationships in HT and UHT metamorphism, the wt.% H<sub>2</sub>O incorporated into melt and cordierite at specified P–T in H<sub>2</sub>O-undersaturated conditions (i.e. Crd+L) and up to H<sub>2</sub>O fluid saturation (i.e. Crd+L+V) are systematically correlated (Harley & Carrington 2001; Harley *et al.* 2002). When considered in terms of  $a_{\text{H}_2\text{O}}$ , a linear relationship exists between  $n/(1-n)$  in cordierite and the  $a_{\text{H}_2\text{O}}$  functions which describe H<sub>2</sub>O uptake in melt as based on the Burnham model (Burnham 1994; Holloway & Blank 1994), but fitted using the H<sub>2</sub>O solubility data of Holtz & Johannes (1994) and Johannes & Holtz (1996). This relationship allows modelling of the variation in  $D_w$ , the distribution of H<sub>2</sub>O between peraluminous granitic melt and cordierite as a function of P–T and  $a_{\text{H}_2\text{O}}$ .  $D_w$  is defined as:

$$D_w = [\text{wt.\% H}_2\text{O}(\text{melt})] / [\text{wt.\% H}_2\text{O}(\text{Crd})] \quad (2)$$

The H<sub>2</sub>O distribution curves presented in Figure 2 are calculated from the models developed by Harley & Carrington (2001) based on their experimental data. At low melt H<sub>2</sub>O contents in the range 1–3.5 wt.% (those likely to be typical of HT/UHT melts),  $D_w$  values are generally in the range 2.5–5.0. As considered in Harley *et al.* (2002) and below, such  $D_w$  values impact on the amount of melt that can be produced in a cordierite-forming dehydration-melting reaction compared with dehydration-melting reactions in which cordierite does not participate.

The incorporation of CO<sub>2</sub> into cordierite and its modelling has been the subject of several investigations based on cordierite–fluid exchange experiments (e.g. Johannes & Schreyer 1981; Kurepin 1985; Le Breton & Schreyer 1993). The



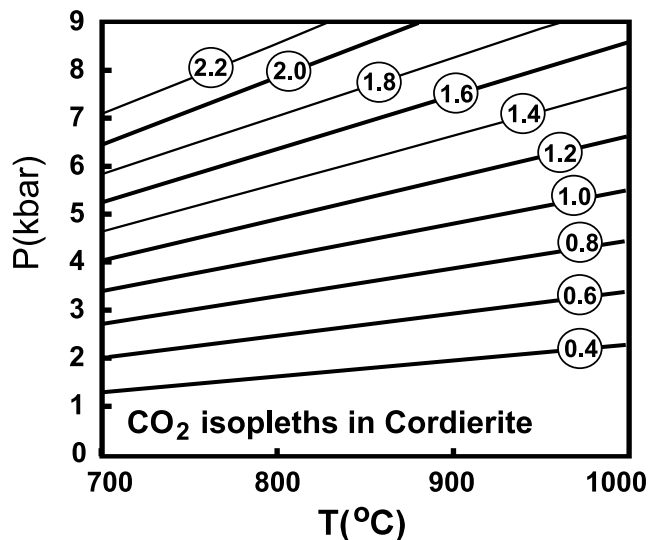
**Figure 2** Modelled distribution curves of H<sub>2</sub>O between cordierite and coexisting granitic melt, calculated from the a-X relationships for cordierite and melt presented by Harley & Carrington (2001), for selected high-temperature P-T conditions (e.g. 2/900 is 2 kbar and 900 °C). Note that  $D_w$  at a selected P-T condition and cordierite H<sub>2</sub>O content can be calculated from this diagram simply by dividing the appropriate wt.% H<sub>2</sub>O (melt) by wt.% H<sub>2</sub>O (Crd). The shaded field depicts the H<sub>2</sub>O contents typical of cordierite coexisting with high-temperature/ultra-high-temperature melts.

exchange experiments have internal inconsistencies and appear to fail to achieve equilibrium (Le Breton & Schreyer 1993), rendering previous modelling tenuous. However, Thompson *et al.* (2001) and Harley *et al.* (2002) have recently reported and summarised the results of cordierite-granitic melt experiments conducted in the presence of mixed H<sub>2</sub>O-CO<sub>2</sub> fluids. Extrapolation of the linear relationships which exist between  $a_{CO_2}$  and  $m/(1-m)$  in these experiments allows calculation of the maximum quantity of CO<sub>2</sub> that can be taken up by cordierite at unit  $a_{CO_2}$  for each P, T condition. The P-T- $a_{CO_2}$  dependence of the incorporation of CO<sub>2</sub> into cordierite P-T range 3–7 kbar and 800–1000 °C is then described by the following equation:

$$a_{CO_2} = [m/(1-m)] \cdot (\exp\{[-3073(\pm 200) + (0.3023P)] / [T + 13.1(\pm 1.2)]\} / f_{CO_2(P,T)} \quad (3)$$

Setting  $a_{CO_2} = 1$  and solving for ‘m’ at specified P-T and  $f_{CO_2}(P,T)$  produces CO<sub>2</sub> isopleths like those presented in Figure 3. Equation 3 and the calculated isopleths, which are consistent with one of the experimental cordierites used by Johannes & Schreyer (1981), are used here in the consideration of the effects of CO<sub>2</sub> on HT/UHT equilibria involving cordierite.

As an independent check on the validity of the cordierite-granitic melt experiments conducted in the presence of mixed H<sub>2</sub>O-CO<sub>2</sub> fluids, the H<sub>2</sub>O contents of melt and CO<sub>2</sub>-bearing cordierite have been measured (Thompson *et al.* 2001). The  $D_w$  calculated from these data (e.g. for a given P-T condition and melt H<sub>2</sub>O content) are consistent with those modelled from the H<sub>2</sub>O-undersaturated experiments of Harley & Carrington (2001). This indicates ideal or near-ideal behaviour of H<sub>2</sub>O and CO<sub>2</sub> in the channel site of cordierite, and furthermore, implies that CO<sub>2</sub> has negligible impact on distribution of H<sub>2</sub>O between melt and cordierite, at least at temperatures of 800 °C and above. In other words, the H<sub>2</sub>O contents of H<sub>2</sub>O-CO<sub>2</sub>-bearing cordierite can be used to deduce the H<sub>2</sub>O contents of any fugitive melts formerly coexisting with cordierite under HT/UHT conditions. This applies so long as the HT/UHT melts



**Figure 3** Pressure-temperature diagram contoured with the isopleths of CO<sub>2</sub> in  $X_{Mg} = 0.80$  cordierite coexisting with pure CO<sub>2</sub> fluid, as modelled by Thompson *et al.* (2001) and Harley *et al.* (2002). The isopleths are expressed in terms of wt.% CO<sub>2</sub>.

are close to the experimental leucogranitic melts in terms of their major element chemistries, such as Na/K and SiO<sub>2</sub> contents (Thompson *et al.* 2002), or can be corrected to account for differences in these parameters. In the present work, the experimental cordierite-melt data will be applied to analyse mineral-melt reaction systematics in KFMASH. This involves correction of the melt H<sub>2</sub>O model to account for the lack of Na. In practice, this correction is very small (<0.5 wt.% H<sub>2</sub>O in melt at saturation: Holtz & Johannes 1994; Johannes & Holtz 1996), and within the error range of the experimental data and model (<0.1 wt.% H<sub>2</sub>O in melt) for the range of low- $a_{H_2O}$  conditions considered in the analysis presented herein.

Equations 1 and 3 allow calculation of the saturation values (molecules p.f.u. or wt.%) of both H<sub>2</sub>O and CO<sub>2</sub> in cordierite at any intermediate H<sub>2</sub>O-CO<sub>2</sub> fluid composition providing an appropriate fluid a-X relation is used for H<sub>2</sub>O-CO<sub>2</sub> mixing. In the present study, as in previous work (Thompson *et al.* 2001; Harley *et al.* 2002), the authors have adopted the same fluid H<sub>2</sub>O-CO<sub>2</sub> a-X model as applied to the experiments, i.e. the CORK model of Holland & Powell (1990). The saturation H<sub>2</sub>O-CO<sub>2</sub> channel fluid contents and channel  $X_{CO_2}$  attainable in cordierite coexisting with peraluminous granitic melts produced through ‘dehydration’ melting in the presence of a low- $a_{H_2O}$ , CO<sub>2</sub>-rich fluid phase will be investigated and tested in comparison with natural rocks, following an analysis of the impact of cordierite volatile contents on melting and phase relations in HT/UHT model systems.

## 2. Impact of cordierite on percentage melting: H<sub>2</sub>O distribution systematics

As noted in the introduction and demonstrated in the seminal work of Waters (1988), dehydration-melting of biotite-bearing mineral assemblages in magnesian pelites ( $X_{Mg} > 0.5$ ) is often controlled by cordierite-forming reactions such as the KFMASH divariant equilibrium:



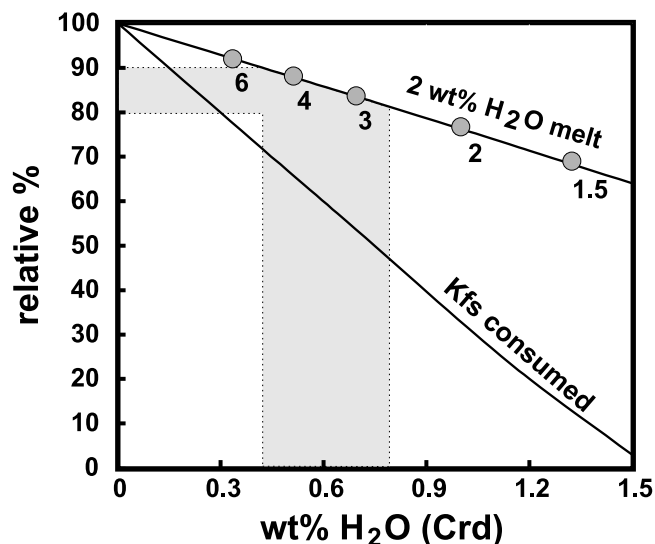
which is related to the KFMASH univariant reaction:



(Fig. 5a). Reaction R2 is also recognised as a multivariant equilibrium controlling melting in more complex natural rock systems and case studies (e.g. Fitzsimons 1996; White *et al.* 2001).

Consideration of cordierite as a H<sub>2</sub>O-bearing phase shows that its formation as a peritectic phase via reaction R1 decreases the volume percentage of melt produced from the dehydration-melting of biotite-bearing pelites. This was first recognised by Harley (1994), who defined the distribution of H<sub>2</sub>O between melt and cordierite (now denoted as  $D_w = \text{wt.}\% \text{H}_2\text{O}_{\text{melt}} / \text{wt.}\% \text{H}_2\text{O}_{\text{crd}}$ ), and suggested, on the basis of one reconnaissance experiment, that this distribution coefficient was  $3.3 \pm 0.5$ . Stevens *et al.* (1995) indirectly produced  $D_w$  values ( $2.1 \pm 0.3$  to  $1.5 \pm 1.1$  at 800–1000°C) for a series of melting experiments at 5 kbar using modal mass-balance calculations, and suggested that the proportion of melt produced would be ‘severely’ restricted. Direct experimental determination of cordierite and melt H<sub>2</sub>O contents (Carrington & Harley 1996; Harley & Carrington 2001) demonstrated that dehydration-melts coexist with cordierites which contain 0.4–1.6 wt.% H<sub>2</sub>O, depending on P–T. Modelling of  $D_w$  as a function of P, T and  $a_{\text{H}_2\text{O}}$  shows that  $D_w$  lies in the range 2.5–5.0 for dehydration melting in the P–T field 5–9 kbar and 850–1000°C (e.g. Fig. 2). Based on mass-balance calculations in KFMASH,  $D_w$  values of this magnitude cause a 15–30% relative decrease in the amount of melt produced from reaction R1 compared with the analogous reaction assuming anhydrous cordierite or with melting reactions involving garnet, which may operate at similar P–T conditions, but in Fe-richer bulk compositions. An example of this behaviour is illustrated in Figure 4, which shows the impact of cordierite wt.% H<sub>2</sub>O on the relative amount of melt produced when that melt contains 2 wt.% H<sub>2</sub>O, corresponding to temperatures of 900–950°C at 5–8 kbar. In this case, the amount of melt is reduced by some 20%. The general conclusion from this is that the amount of melt produced from slightly more magnesian, cordierite-bearing pelites will be less than that produced from garnet-bearing pelite at the same P–T conditions – the cordierite-bearing lithologies will appear more refractory.

Using the same logic, for a specific bulk rock composition, the amount of melt produced at lower-P where cordierite is stable in preference to garnet in a pelite with intermediate  $X_{\text{Mg}}$  (=0.40–0.60) will be some 20% (relative) less than that predicted from analyses which ignore the impact of cordierite H<sub>2</sub>O on the stoichiometry of the melting reactions. Moreover, since K-feldspar is consumed in proportion to the amount of melt produced (Fig. 4), some 50% (relative) less K-feldspar is consumed in the cordierite-bearing case. Hence, K-feldspar will persist to higher temperatures if it initially is present in similar modal amounts in Mg- and Fe-pelites. These considerations also apply to all calculations of pseudosections involving cordierite at HT/UHT conditions (e.g. White *et al.* 2001; Kelsey *et al.* 2003). Decreased melt production means that K-feldspar will persist to higher-T, and hence, be able to participate in osumilite-forming reactions; for example, in bulk compositions which otherwise may be modelled to lose K-feldspar, and hence, not intersect potential osumilite-producing reactions, such as those depicted in Figure 5a. Hence, consideration of cordierite as a phase that sequesters H<sub>2</sub>O in the melting regime extends the range of KFMASH bulk compositions (in terms of A<sup>\*</sup>KF) which are accessible to osumilite. Pseudosections which attempt to illustrate the mineral assemblages stable with melt in specific pelite rock compositions in HT/UHT metamorphism must recognise and incorporate the effect of H<sub>2</sub>O in cordierite on the percentage

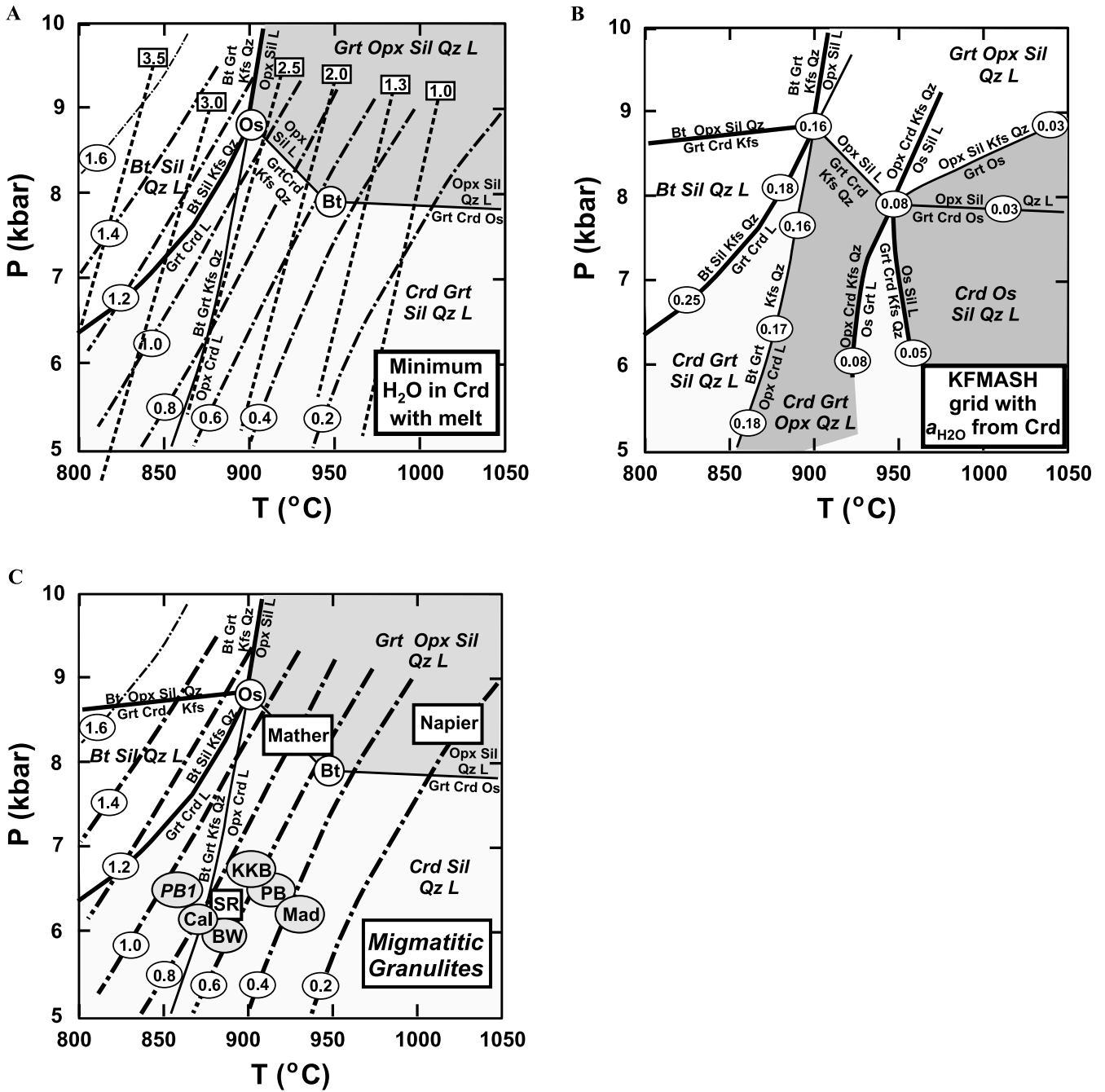


**Figure 4** Relative proportion of melt produced and K-feldspar consumed (normalised to 1 for the case of anhydrous cordierite) in a model pelite initially containing 25% biotite for the case in which the P–T conditions of melting result in a melt with 2 wt.% H<sub>2</sub>O (e.g. 5.5 kbar/900°C to 9.5 kbar/950°C; see Fig. 5a). The relative proportions of melt produced and K-feldspar consumed in the reaction (R1) decrease as the H<sub>2</sub>O-content of coexisting cordierite increases and  $D_w$  (numbers below filled circles) decreases [i.e. as P increases along the 2 wt.% H<sub>2</sub>O (melt) isopleth in Fig. 5a]. The shaded field depicts the H<sub>2</sub>O contents typical of cordierite in this case, which lead to a decrease in melt production to 80–90% of the amounts expected if the H<sub>2</sub>O content of cordierite is ignored.

melt production and residual solid phase assemblage if they are to be realistic and informative.

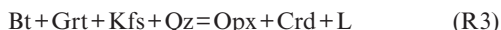
### 3. Integration of cordierite-melt H<sub>2</sub>O data with UHT reaction grids: predicted cordierite H<sub>2</sub>O contents and $a_{\text{H}_2\text{O}}$ conditions in HT/UHT metamorphism

The H<sub>2</sub>O contents of cordierite coexisting with melt, and the  $a_{\text{H}_2\text{O}}$  conditions along KFMASH dehydration-melting reactions involved in HT/UHT metamorphism (Carrington & Harley 1995a; Harley 1998a; White *et al.* 2001; Kelsey *et al.* 2003), can be calculated based on knowledge of the variation in the minimum H<sub>2</sub>O content of peraluminous granitic melt with P, T and  $D_w$  over the same P–T domain (Harley & Carrington 2001). Contours of minimum melt H<sub>2</sub>O contents (Holtz & Johannes 1994; Johannes & Holtz 1996) are superimposed on the KFMASH petrogenetic grid involving the phases Grt, Crd, Bt, Sil, Opx, Qz, Kfs, L and Os developed by Carrington & Harley (1995a, b) and modified in the light of calculations by subsequent workers (Holland *et al.* 1996; White *et al.* 2001; Kelsey *et al.* 2003) in Figure 5a. Using the  $D_w$  relationships implicit in Figure 2 and described in Harley & Carrington (2001), this grid also has been contoured for the H<sub>2</sub>O content of cordierite coexisting with these dehydration-melts. Like the melt H<sub>2</sub>O content isopleths, but in contrast to cordierite H<sub>2</sub>O saturation isohydrans, the cordierite H<sub>2</sub>O isopleths relevant to dehydration melting are strongly temperature-dependent, varying from 1.2 to 1.4 wt.% H<sub>2</sub>O at 800°C to less than 0.2 wt.% H<sub>2</sub>O at 1000°C. Moreover, comparison of these isopleths with the assemblage fields defined by the KFMASH grid shows that cordierites coexisting with dehydration melts in the assemblage Bt+Sil+Crd+Qz+Kfs+L should generally contain >1.2 wt.% H<sub>2</sub>O (melt H<sub>2</sub>O >3 wt.%), whereas cordierites in the higher-T migmatite



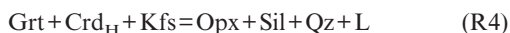
**Figure 5** (A) Contoured pressure–temperature (P–T) diagram depicting cordierite–melt H<sub>2</sub>O relationships for conditions where the melt has its minimum possible H<sub>2</sub>O content at P and T. Contours of minimum melt wt.% H<sub>2</sub>O (dashed lines annotated with wt.% H<sub>2</sub>O values in rectangles) are after Johannes & Holtz (1996) and Harley & Carrington (2001). Contours of cordierite wt.% H<sub>2</sub>O (dot-dashed lines annotated with wt.% H<sub>2</sub>O values in ellipses) are derived from the  $D_w$ - $a_{H_2O}$  relationships defined in Harley & Carrington (2001) and calculated using Equation 1 for  $a_{H_2O}$  compatible with those defined by the melt isopleths. The heavy solid lines are KFMASH system reactions which limit the stabilities of key cordierite-bearing assemblages (e.g. Crd+Grt+Sil+Qz+L). These reactions are based on Carrington & Harley (1995a), as modified by White *et al.* (2001), and are focused on the osmilite-absent, [Os], and biotite-absent, [Bt], invariant points (see Fig. 5b for other related KFMASH equilibria). (B) A P–T diagram depicting KFMASH system reactions based on Carrington & Harley (1995a, b), as modified by White *et al.* (2001), and focused on the osmilite-absent, [Os], and biotite-absent, [Bt], invariant points of Fig. 5a. These invariant points have associated  $a_{H_2O}$  values of 0.16 and 0.08 respectively (see text for discussion). Selected KFMASH reactions are labelled at specific P–T conditions for  $a_{H_2O}$  calculated from the modelled cordierite H<sub>2</sub>O contents (Harley & Carrington 2001; see Fig. 5a). Selected mineral assemblage fields are illustrated by shading. (C) A P–T diagram as in Figure 5a, contoured for the H<sub>2</sub>O contents of cordierite formed in equilibrium with KFMASH granitic melt, illustrating the P–T conditions of equilibration of the Crd+Sil migmatites (ellipses) and Crd+Opx migmatites/granulites (rectangles) listed in Table 1. The P–T conditions inferred from independent equilibria are in reasonable agreement with measured cordierite H<sub>2</sub>O contents in most cases (Mad: Madagascar; KKB: Kerala Khondalite Belt; Cal: Calabria; BW: Bayerische Wald; SR: Strangways Range; Mather; Napier), but peak temperature estimates for Prydz Bay (PB1) are significantly lower than would be deduced from cordierite in this case (PB). Sources for P–T estimates are given in Table 1 along with the relevant cordierite compositional data.

assemblage Grt+Crd+Sil+Qz+Kfs+L should preserve H<sub>2</sub>O contents in the range 1.1–0.2 wt.%, depending on T. Cordierite in the assemblage Crd+Opx+Qz+Kfs+L, which lies to higher-T than the KFMASH univariant:



is constrained to contain <0.8 wt.% H<sub>2</sub>O for all UHT P–T conditions apart from those near the [Os] invariant point at 8.8 kbar and ca. 900 °C.

The volatile content of cordierite formed through dehydration-melting is critical to the stability of cordierite+garnet with respect to assemblages such as orthopyroxene+sillimanite+quartz and sapphirine+quartz (Aranovich & Podlesskii 1989; Bertrand *et al.* 1991; Carrington 1995; Carrington & Harley 1995a; Holland *et al.* 1996; Aranovich & Berman 1996). As shown in Figure 5a, a pronounced change in melt H<sub>2</sub>O contents in the 900–950 °C interval coupled with an increase in  $D_w$  from 2.4 to 3.0 leads to a marked decrease in cordierite H<sub>2</sub>O from 1.1 to 0.5 wt.% along the univariant reaction that joins the two invariant points equivalent to [Os] and [Bt] in the grid of Carrington & Harley (1995a), and limits the stability of Fe-Mg garnet+cordierite in this system:



where Crd<sub>H</sub> denotes hydrous cordierite in equilibrium with the dehydration melt. The negative dP/dT slope of this reaction is consistent with and, at least in part, reflects this marked decrease in channel occupancy. Cordierite that persists with Opx+Sil+L at pressures above those of reaction R4 is predicted to contain 1.1–0.4 wt.% H<sub>2</sub>O over the temperature range 900–970 °C. It is also clear from Figure 5a that cordierite coexisting with osumilite can only contain up to 0.5 wt.% H<sub>2</sub>O and would generally contain less (<0.4 wt.%) in UHT terrains.

Using Equation 1,  $a_{\text{H}_2\text{O}}$  along the dehydration-melting reactions and at the invariant points in the KFMASH grid (Carrington & Harley 1995a; Holland *et al.* 1996) has been calculated (Fig. 5b). These  $a_{\text{H}_2\text{O}}$  values vary from 0.24 at 6.7 kbar and 825 °C to 0.16 at 8.8 kbar and 900 °C in the case of Reaction R2, and from 0.18 at 5 kbar to 0.16 at 8.8 kbar along the very steep (dP/dT=85 bar/°C) Reaction R3. The  $a_{\text{H}_2\text{O}}$  values calculated for the two key KFMASH invariant points using the present authors' cordierite and melt models are 0.16 ± 0.03 at the lower-T [Os] point (8.8 kbar/900 °C), and only 0.08 ± 0.02 at the [Bt] point (7.9 kbar/940 °C) where the osumilite+garnet assemblage becomes stable and overlaps with assemblages involving orthopyroxene+sillimanite+quartz+melt (Carrington & Harley 1995b). From this, we can infer that the osumilite-bearing assemblages equilibrated at 7–9 kbar in the Napier Complex of East Antarctica (Ellis *et al.* 1980; Grew 1982; Audibert *et al.* 1995) and other UHT terrains imply  $a_{\text{H}_2\text{O}}$  of <0.08.

The contoured KFMASH melting grids (Fig. 5a, b) are consistent with independent P–T estimates obtained from garnet+cordierite+sillimanite migmatitic granulites from the Kerala Khondalite Belt (Nandakumar & Harley 2000), southern Madagascar (Markl *et al.* 2000) and Calabria (Schenk 1984). SIMS H<sub>2</sub>O measurements on cordierites from these terrains yield  $a_{\text{H}_2\text{O}}$  conditions in the range 0.06–0.18 (Table 1) and imply cordierite-melt equilibrium at P–T conditions in the range ca. 6–7 kbar and 860–930 °C, depending on terrain (Fig. 5c). The H<sub>2</sub>O contents of former melts which equilibrated with these low-H<sub>2</sub>O (0.6–1.2 wt.%) cordierites are 1.3–2.2 wt.%. Based on measured cordierite CO<sub>2</sub> contents, calculated  $a_{\text{CO}_2}$  in these migmatitic granulites are high (0.34–0.85) but consistent with fluid-undersaturation in all examples except Calabria. This is considered further in section 5 below.

The H<sub>2</sub>O contents of cordierites from cordierite-sillimanite migmatites from the Bayerische Wald have been determined by informed spectroscopy (IR) techniques by Kalt (2000). The average H<sub>2</sub>O content of cordierite based on all the measured samples in this case is 0.53 ± 0.10 wt.%, although one sample preserves cordierite with up to 0.74 wt.% H<sub>2</sub>O. This most hydrous cordierite is consistent with equilibrium with granitic melt containing 2.5 wt.% H<sub>2</sub>O at the upper end of the P–T conditions preferred by Kalt (2000) for the metamorphic peak in this region based on geothermobarometric calculations (BW, Fig. 5c.: ca. 6 kbar, 870 °C). The majority of samples which preserve lower H<sub>2</sub>O contents could be interpreted to indicate melt loss at higher temperatures (up to 900 °C), but could equally reflect post-peak loss or leakage of H<sub>2</sub>O from the cordierite channels in this case.

A similar interpretation could be put forward for cordierites in the garnet+cordierite+sillimanite migmatitic granulites of Prydz Bay, East Antarctica (Fitzsimons 1994, 1996). The H<sub>2</sub>O contents, measured by SIMS, of these cordierites are only 0.35–0.60 wt.% and average at ca. 0.5 wt.% (Table 1; Harley *et al.* 2002). Such low H<sub>2</sub>O contents would be consistent with cordierite-melt equilibrium at 6.5 kbar and 900–930 °C (PB, Fig. 5c), whereas geothermometry corrected for the effects of Fe-Mg exchange and phase equilibrium considerations indicate peak temperatures of 860 °C (Fitzsimons 1996). If the latter temperatures are accepted (PBI, Fig. 5c) then the cordierite that coexisted with melt according to Figure 5c would have contained >0.8 wt.% H<sub>2</sub>O, implying that all of the cordierites measured from the Prydz Bay granulites have lost between 25% and 50% of their initial H<sub>2</sub>O. Such marked H<sub>2</sub>O loss is not required to explain the volatile contents and phase relations of most of the other examples considered here and in Harley *et al.* (2002), particularly in the cases where the cordierites contain significant CO<sub>2</sub> (e.g. BB4: 0.6 wt.% CO<sub>2</sub>). Hence, although the present authors cannot discount the possibility that some H<sub>2</sub>O leakage has occurred from cordierite, they suggest that the peak temperatures attained in the Prydz Bay granulites were higher than those deduced by Fitzsimons (1996) and in the range 900–930 °C.

Also depicted in Figure 5c are the preferred P–T conditions for three examples of cordierite-orthopyroxene HT/UHT granulites. Migmatitic garnet+orthopyroxene+cordierite granulite from Strangways Range (Arunta Complex) and garnet+orthopyroxene+cordierite ± sillimanite granulite from Mather Peninsula (Harley 1998b) both lie on the 0.7 wt.% H<sub>2</sub>O isopleth and indicate temperatures wholly consistent with independent estimates from geothermobarometry. At UHT conditions of greater than 1000 °C at 8–9 kbar, as recorded from several localities in the Napier Complex of East Antarctica (Ellis *et al.* 1980; Sheraton *et al.* 1987; Harley & Hensen 1990; Harley & Motoyoshi 2000),  $a_{\text{H}_2\text{O}}$  values calculated using cordierite-melt equilibria (Fig. 5b; Table 1) are only 0.04–0.02. Any cordierite stable in osumilite-bearing assemblages, or with sapphirine+quartz in the presence of melt, would be expected to have H<sub>2</sub>O contents of only 0.2 wt.%; lower H<sub>2</sub>O cordierites would be present if melting did not occur. Two samples from the Napier Complex preserve cordierites containing 0.2 wt.% H<sub>2</sub>O (Table 1), consistent with this expectation (Fig. 5c).

#### 4. Melting and migmatization in the H<sub>2</sub>O-CO<sub>2</sub> system

So far, the present authors have considered only the impact of cordierite as a H<sub>2</sub>O-bearing phase involved in melting and

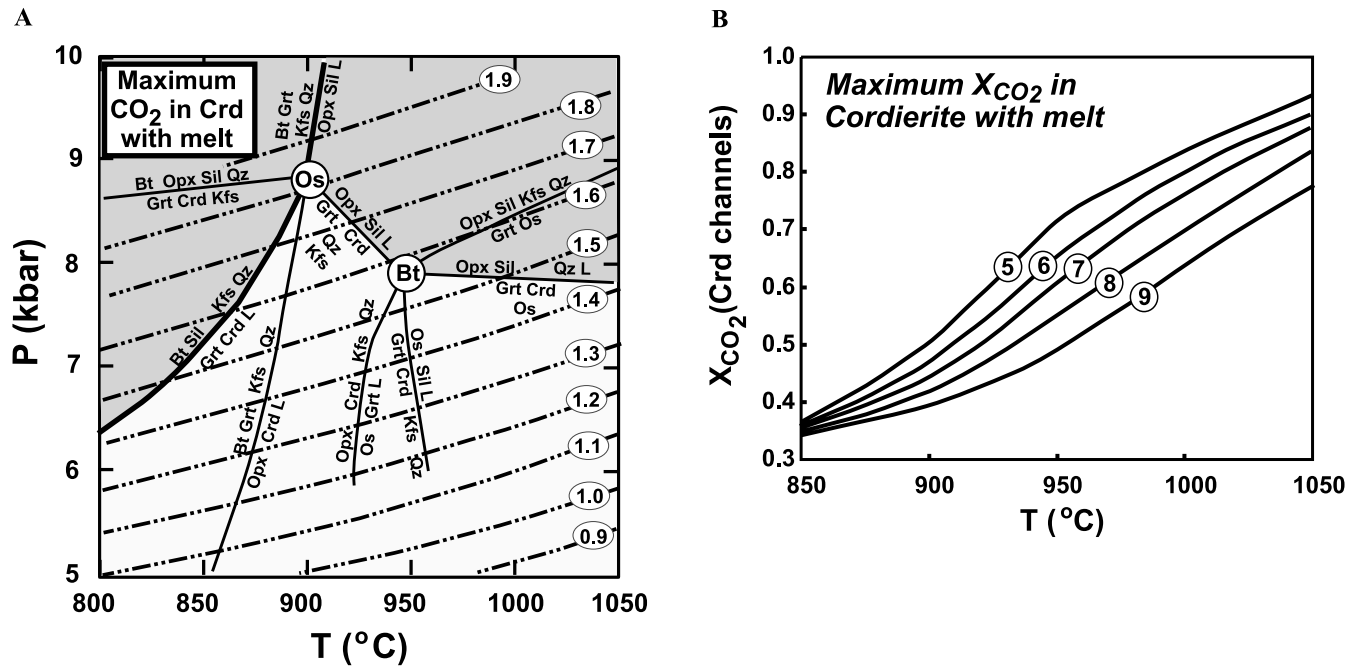
**Table 1** Volatiles in cordierites from selected high-temperature and ultra-high-temperature granulites/migmatites\*

Sample	Cordierite							P (kbar)	T (°C)	$a_{\text{H}_2\text{O}}$	$a_{\text{CO}_2}$	Melt	
	$X_{\text{Mg}}$ (Crd)	H <sub>2</sub> O (wt.%)	CO <sub>2</sub> (wt.%)	n (pfu)	m (pfu)	m+n (pfu)	$X_{\text{CO}_2}$					H <sub>2</sub> O wt.%)	$D_w$
Bayerische Wald (Kalt 2000)													
BW-44ii	0.60	0.740	0.051	0.255	0.007	0.262	0.027	6.0	900	0.178	0.033	2.5	3.3
BW-average	0.60	0.528	0.064	0.180	0.009	0.189	0.048	6.0	900	0.115	0.041	1.8	3.5
Crd-Sil migmatite		<i>0.095</i>	<i>0.018</i>	<i>0.032</i>	<i>0.003</i>	<i>0.032</i>	<i>0.013</i>			<i>0.025</i>	<i>0.012</i>	<i>0.3</i>	
Prydz Bay migmatitic granulites, Antarctica (Fitzsimons 1994, 1996)													
BB4 (17)	0.66	0.494	0.583	0.168	0.081	0.250	0.325	6.0	860	0.096	0.361	1.7	3.5
Grt-Crd-Sil migmatite		<i>0.090</i>	<i>0.118</i>	<i>0.031</i>	<i>0.016</i>	<i>0.038</i>	<i>0.045</i>			<i>0.028</i>	<i>0.122</i>	<i>0.4</i>	
Calabria, Serre Massif (Schenk 1984)													
8-90 (170)	0.63	0.805	1.305	0.272	0.181	0.453	0.400	6.5	875	0.162	0.853	2.2	2.7
Grt-Crd-Sil migmatite		<i>0.060</i>	<i>0.060</i>	<i>0.021</i>	<i>0.008</i>	<i>0.027</i>	<i>0.014</i>			<i>0.014</i>	<i>0.041</i>	<i>0.4</i>	
Kerala Khondalite Belt, Southern India (Nandakumar & Harley 2000)													
SHED10 (10)	0.60	0.636	0.854	0.219	0.120	0.340	0.355	6.5	900	0.129	0.557	2.0	3.1
Grt-Crd leucosome		<i>0.036</i>	<i>0.022</i>	<i>0.012</i>	<i>0.006</i>	<i>0.010</i>	<i>0.011</i>			<i>0.013</i>	<i>0.019</i>	<i>0.3</i>	
Chittikara-SLH (12)	0.60	0.633	0.762	0.218	0.108	0.326	0.330	6.5	900	0.128	0.490	2.0	3.1
Grt-Crd leucosome		<i>0.112</i>	<i>0.053</i>	<i>0.039</i>	<i>0.012</i>	<i>0.020</i>	<i>0.043</i>			<i>0.030</i>	<i>0.043</i>	<i>0.6</i>	
SE Madagascar (Markl <i>et al.</i> 2000)													
patch migmatite (8)	0.86	0.287	0.527	0.095	0.072	0.167	0.431	6.0	920	0.057	0.344	1.3	4.5
Crd leucosome		<i>0.050</i>	<i>0.065</i>	<i>0.017</i>	<i>0.009</i>	<i>0.022</i>	<i>0.029</i>			<i>0.016</i>	<i>0.074</i>	<i>0.3</i>	
Strangways Range, Arunta Complex													
9052 (5)	0.87	0.690	0.023	0.229	0.003	0.232	0.014	6.0	875	0.147	0.013	2.3	3.3
Grt-Opx-Crd patch		<i>0.092</i>	<i>0.005</i>	<i>0.031</i>	<i>0.001</i>	<i>0.031</i>	<i>0.004</i>			<i>0.030</i>	<i>0.004</i>	<i>0.3</i>	
Mather Peninsula, Rauer Islands (Harley 1998b)													
SH/88/218 (8)	0.88	0.698	0.055	0.233	0.008	0.241	0.031	8.5	920	0.091	0.021	1.8	2.6
Grt-Opx-Crd-Sil		<i>0.067</i>	<i>0.021</i>	<i>0.022</i>	<i>0.003</i>	<i>0.024</i>	<i>0.008</i>			<i>0.009</i>	<i>0.011</i>	<i>0.3</i>	
Napier Complex, Enderby Land (Harley, 1986; Sheraton <i>et al.</i> 1987)													
49752 Mt Sones (8)	0.88	0.194	0.498	0.064	0.068	0.132	0.513	8.5	1000	0.025	0.256	0.85	4.4
Grt-Spr-Sil-Crd		<i>0.021</i>	<i>0.026</i>	<i>0.007</i>	<i>0.004</i>	<i>0.010</i>	<i>0.018</i>			<i>0.008</i>	<i>0.024</i>	<i>0.1</i>	
49354 Mt Hardy (6)	0.90	0.215	1.040	0.072	0.142	0.214	0.664	8.5	1000	0.028	0.576	0.96	4.3
Spr-Qz-Crd		<i>0.031</i>	<i>0.021</i>	<i>0.010</i>	<i>0.003</i>	<i>0.013</i>	<i>0.026</i>			<i>0.011</i>	<i>0.025</i>	<i>0.1</i>	

(number) number of SIMS volatile analyses of cordierite in the sample. The  $P$ - $T$  estimates used in the calculation of fluid activities are taken from the references given for each case study. Figures given in italics are the  $1\sigma$  uncertainties in the quoted parameters, propagated from  $1\sigma$  uncertainties in the analytical populations and SIMS calibrations, and uncertainties in the cordierite activity calibrations of Equations 4 and 8, together with  $\pm 0.5$  kbar and  $\pm 30^\circ\text{C}$  uncertainties in the  $P$ - $T$  estimates used in calculation of fluid activities.

mineral reactions in HT/UHT metamorphism and anatexis. However, cordierite also incorporates CO<sub>2</sub> into its channels, and as noted by Thompson *et al.* (2001), the distribution of CO<sub>2</sub> between melt and cordierite is strongly in favour of cordierite, such that  $D_C < 0.2$  and probably  $< 0.1$ . The stability of cordierite as a H<sub>2</sub>O-CO<sub>2</sub>-bearing phase coexisting with melt and preferentially fractionating CO<sub>2</sub> has important consequences for the character of fluid-melt-rock interactions since the melt segregates, migrates and crystallises in granulite host rocks. This can be demonstrated by consideration of the crystallisation of two initially slightly fluid-undersaturated leucogranitic melts (e.g. 2 wt.% H<sub>2</sub>O, 1000 ppm CO<sub>2</sub> at 5 kbar/900°C) which differ only in their  $X_{\text{Mg}}$  [i.e. Mg/(Mg+Fe)]. Cooling of the Fe-richer melt (e.g.  $X_{\text{Mg}}=0.25$ ) will result in the crystallisation of garnet along with quartz and feldspars at these pressures, continuously enriching the remaining melt in both H<sub>2</sub>O and CO<sub>2</sub> until saturation is reached and a CO<sub>2</sub>-rich fluid phase is generated. This fluid may be trapped as CO<sub>2</sub>-rich but post-peak fluid inclusions in garnet, as seen in some migmatites (e.g. Santosh 1987), or it may react with reduced minerals to precipitate graphite as crystallisation proceeds (e.g. Fitzsimons & Matthey 1995). In contrast, crystallisation of a Mg-richer melt (e.g.  $X_{\text{Mg}}=0.35$ ) to form cordierite plus quartz and feldspars will result in a slower increase in melt

H<sub>2</sub>O (dependent on  $D_w$ ) and a decrease in ppm CO<sub>2</sub> in the melt – the latter effect caused by the sequestering of CO<sub>2</sub> by cordierite (at least 5000 ppm CO<sub>2</sub> cf. 500–1000 ppm in the melt). The cordierite-bearing melt or leucosome is unlikely to attain fluid saturation unless external fluids are introduced or rapid decompression occurs, whereby both melt and cordierite exceed their saturation isopleths. In a closed system (i.e. melt batch crystallising in isolation) or in a system in which melt is continuously in communication with cordierite, it is likely that all the available CO<sub>2</sub> will be taken up in the cordierite, inhibiting the formation of fluid inclusions, and indeed, of graphite, since fluid-present conditions are not attained. Conversely, if fluid inclusions (Santosh *et al.* 1993) or leucosome-hosted graphite (Fitzsimons & Matthey 1995) are observed in cordierite-bearing migmatites, it is almost certain that externally derived fluid has been introduced into the system. In principle, such fluid-present conditions should be recorded by the volatile abundances in the cordierite and the  $a_{\text{H}_2\text{O}}$  and  $a_{\text{CO}_2}$  values calculated using Equations 1 and 2. In short, it is significantly more difficult to saturate a cordierite-bearing migmatite terrain than a garnet-dominated migmatite area which lacks cordierite; for similar  $P$ - $T$  conditions and percentage melting, higher fluid fluxes are required in the cordierite migmatite case.



**Figure 6** (A) Pressure-temperature (P-T) diagram showing isopleths of the *maximum* CO<sub>2</sub> contents (in wt.%) in cordierite coexisting with melts with minimum H<sub>2</sub>O contents (i.e. melts with H<sub>2</sub>O contents drawn in Fig. 5a). These isopleths are calculated using Equation 3 (based on Harley *et al.* 2002) in combination with Equation 1. Note that, since cordierite also contains H<sub>2</sub>O, which varies mainly with temperature (Fig. 5a), these CO<sub>2</sub> isopleths do not correspond to those presented for the pure CO<sub>2</sub> system in Figure 3. (B) The *maximum* X<sub>CO<sub>2</sub></sub> composition of cordierite coexisting with melt and a free-CO<sub>2</sub>-dominated fluid phase, plotted as a function of temperature in the melting range for various pressures (in kilobars; denoted by numbers in circles). Cordierite coexisting with a low-H<sub>2</sub>O melt at 950°C and 7 kbar may contain up to 1.4 wt.% CO<sub>2</sub> (Fig. 6a) and have a channel X<sub>CO<sub>2</sub></sub> of up to 0.6 without fluid saturation being attained.

## 5. The effect of CO<sub>2</sub> in cordierite on KFMASH equilibria in HT/UHT metapelites

The contoured grid presented in Figure 5a only includes H<sub>2</sub>O dissolved in melt and incorporated in cordierite. If CO<sub>2</sub> is added to this system, it is favourably incorporated into cordierite compared with melt, as noted above, and all other solid phases in the absence of graphite. Given that only  $a_{\text{H}_2\text{O}}$  is fixed, at fixed P-T, by the dehydration melting reactions of Figure 5a, it is possible for cordierites with near-constant H<sub>2</sub>O contents but a range of CO<sub>2</sub> contents to be in equilibrium with melts with near-minimum H<sub>2</sub>O contents in the KFMASH-CO<sub>2</sub> system. The upper limit on the CO<sub>2</sub> content of cordierite coexisting with melt is that calculated for fluid saturation, but cordierites with low H<sub>2</sub>O contents and elevated CO<sub>2</sub> contents which are still less than those required for saturation could coexist with melt alone under fluid-absent conditions.

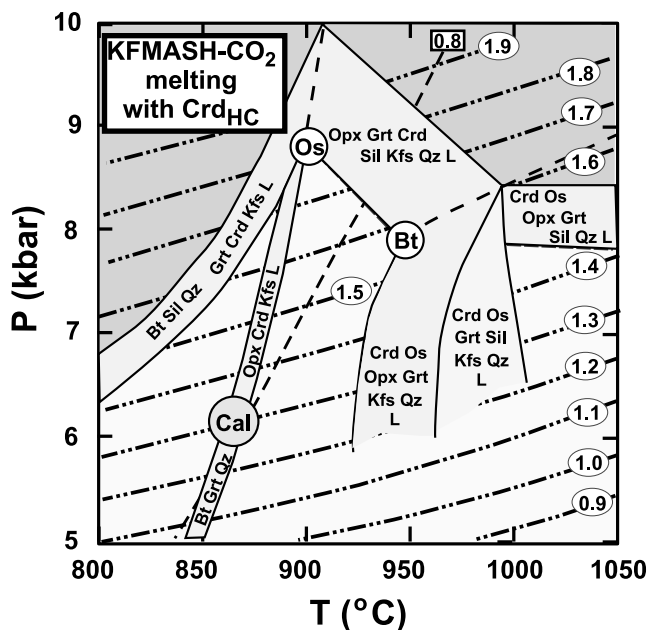
The maximum (saturation) CO<sub>2</sub> contents of cordierite coexisting with melts formed through biotite dehydration melting are presented as wt.% CO<sub>2</sub> contours in Figure 6a. These isopleths are steeper than and differ from those presented in Figure 3 since they are calculated for fluid saturation in the H<sub>2</sub>O-CO<sub>2</sub> system in which  $a_{\text{H}_2\text{O}}$ , and hence, cordierite H<sub>2</sub>O content is defined by Crd+L equilibrium. Hence, at lower temperatures, where both cordierite and melt have higher H<sub>2</sub>O contents (Fig. 5a), the maximum CO<sub>2</sub> contents attainable in the melt environment are significantly less than those defined for the CO<sub>2</sub>-only system of Figure 3, whereas, under HT/UHT conditions, the Crd-L-V isopleths approach those in the CO<sub>2</sub>-only system. This is further illustrated by the cordierite channel H<sub>2</sub>O-CO<sub>2</sub> composition diagram of Figure 6b, which shows that cordierites with channel X<sub>CO<sub>2</sub></sub> of up to 0.4 may coexist with melt at 900°C, whilst, at 1000°C, the cordierite channel X<sub>CO<sub>2</sub></sub> can be as high as 0.6–0.7. The presence of CO<sub>2</sub>-rich, high-X<sub>CO<sub>2</sub></sub> cordierite does not automatically imply the presence

of a free carbonic fluid phase in UHT metamorphism or in HT migmatites (Vry *et al.* 1990; Fitzsimons 1994; Harley 1994).

If CO<sub>2</sub> is added to the KFMASH system without the addition of a separate new phase, its favourable incorporation into cordierite will enhance the stability of the mineral, even at fixed  $a_{\text{H}_2\text{O}}$ , and cause all other KFMASH univariant reactions to slide along loci which coincide with the cordierite-absent reactions emanating from the KFMASH invariant points (Carrington 1995). For the H<sub>2</sub>O-CO<sub>2</sub> system, Thompson *et al.* (2001, 2002) and Harley *et al.* (2002) have shown that the minimum solubility of H<sub>2</sub>O in granitic melt is essentially independent of the CO<sub>2</sub> content of the system and that  $D_w$  (Crd-L) is similar at a given melt H<sub>2</sub>O content to the H<sub>2</sub>O-only system. Hence, the dehydration-melting isopleth sets (Crd and L wt.% H<sub>2</sub>O contours) of Figure 5a shift very little with the addition of CO<sub>2</sub> into the cordierite. This behaviour does not apply to saturation H<sub>2</sub>O isopleths because, in that case, there is an overall decrease in total volatiles in cordierite at a given P-T as CO<sub>2</sub> enters its channels.

With the addition of CO<sub>2</sub> into cordierite, the KFMASH [Os] and [Bt] points move to higher P and T along (Crd) reactions whereas the H<sub>2</sub>O-isopleths remain fixed. Hence, the stability fields of Grt+Crd+Sil+Kfs+Qz+L and Grt+Opx+Crd+Kfs+Qz+L expand to higher pressure, and to both higher and lower temperatures, and KFMASH-C divariant melting fields are generated from the KFMASH univariant dehydration-melting reactions (Fig. 7). Under UHT conditions (>900°C), the high-P stability of Grt+Crd+L, which is bounded up-pressure by the assemblage Opx+Sil+Qz+L, is estimated to be extended by at least 1 kbar on the basis of comparisons between the experimental data of Carrington & Harley (1995a, b) and Bertrand *et al.* (1991), and calculations by Aranovich & Podlesskii (1989). Paradoxically, the addition of CO<sub>2</sub> to the H<sub>2</sub>O-undersaturated (dehydration-melting)

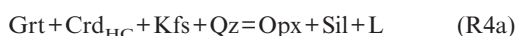




**Figure 7** Pressure–temperature (P–T) diagram depicting the offset of selected KFMASH system reactions focused on the [Os] and [Bt] points of Figure 5a as a consequence of the addition of CO<sub>2</sub> to produce the system KFMASH–CO<sub>2</sub>. Note that the KFMASH invariant points become lines located along (Crd) equilibria, sliding up–pressure with increasing CO<sub>2</sub> in cordierite. KFMASH univariant reactions become seven phase divariant fields in which cordierite can vary in H<sub>2</sub>O and CO<sub>2</sub> depending on P–T (shaded fields). The maximum CO<sub>2</sub> contents of cordierite in these fields are dictated by the isopleths shown (dot-dashed contours in wt.%), which define CO<sub>2</sub> at the offset boundaries of the fields. For example, cordierite in the field Crd+Os+Opx+Grt+Kfs+Qz+L will contain 1.4 wt.% CO<sub>2</sub> at 7.3 kbar, 960°C. Also shown on this diagram is the preferred P–T estimate for the Calabrian cordierite, Cal, which contains 0.8 wt.% H<sub>2</sub>O and 1.3 wt.% CO<sub>2</sub> (Table 1). This cordierite lies on the saturation CO<sub>2</sub> isopleth, and hence, suggests equilibration in the presence of melt plus CO<sub>2</sub>-rich fluid at ca. 6 kbar and 860°C.

system decreases the temperature of melting, as controlled by the melting reactions which emanate down–pressure from the [Os] point, i.e. melting via equilibria such as R2 and R1 proceeds at lower temperatures in the fluid-saturated and -undersaturated H<sub>2</sub>O–CO<sub>2</sub> systems compared with the H<sub>2</sub>O-only one, not as a result of CO<sub>2</sub> entering the melt, but rather, reflecting the stabilisation of cordierite, the solid product of the peritectic melting reactions. By stabilising cordierite, it is possible for divariant melting in the presence of a CO<sub>2</sub>-rich fluid to progress at temperatures some 20–40°C lower than those required for melting via the reactions noted above (Fig. 7), provided enough H<sub>2</sub>O is available to ensure the melt does not crystallise. In other words, the *a*<sub>H<sub>2</sub>O</sub> must be at least as high as that value defined by the dehydration–melting reaction at the proscribed P–T condition.

The movement of the KFMASH invariant points to higher P also have consequences for the range of volatile compositions attainable by cordierite coexisting with melt. The displaced [Os] point will occur at higher *a*<sub>H<sub>2</sub>O</sub> and as a result, the cordierite and melt will both have higher H<sub>2</sub>O contents (ca. 1.2 and 3 wt.%, respectively) at the saturation condition where CO<sub>2</sub> is in excess but in equilibrium with both Crd and L (10 kbar, 910°C in Fig. 7). The [Bt] point displaces to higher P and T, and therefore, will involve cordierite and melt with marginally lower H<sub>2</sub>O contents (0.2 and 1 wt.%, respectively), but the cordierite will have high CO<sub>2</sub> (1.6 wt.%; Fig. 7). As a consequence of these displacements, the high-P limiting reaction involving H<sub>2</sub>O–CO<sub>2</sub> cordierite (Crd<sub>HC</sub>):



occurs at higher pressures and over a broader T range (900–1000°C) in the CO<sub>2</sub>-bearing system compared with the KFMASH case, and at ca. 10–9 kbar (Fig. 7). At saturation (high CO<sub>2</sub>, low *a*<sub>H<sub>2</sub>O</sub>, melt still present), this reaction may have a flat to moderately negative dP/dT, dictated by the change in H<sub>2</sub>O–CO<sub>2</sub> partitioning between Crd and V across this T range. In the absence of relevant partitioning data, this reaction is drawn parallel to R4 in Figure 7.

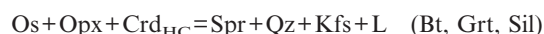
### 6. Consequences for the stability of osumilite in melt-bearing UHT rocks

The uptake of CO<sub>2</sub> by cordierite and its consequent stabilisation to higher P relative to Opx+Sil+Qz has implications for the stability of osumilite and Os+Grt assemblages which may be developed in appropriate KFMASH bulk rock compositions (high-Mg, aluminous) along with melt under UHT conditions (Audibert *et al.* 1995; Carrington & Harley 1995b; Holland *et al.* 1996; White *et al.* 2001). The P–T stability field occupied by osumilite in KFMASH is limited by reactions focused on the [Bt] invariant point (Fig. 5a). Translation of this point up–pressure by a minimum of 0.5 kbar to 8.4 kbar and 990°C, expands the stability field of Grt+Crd +Os+L towards higher pressures. However, the stability fields of Os+Sil+L and Os+Grt+L contract to higher T at pressures less than those of the [Bt] point (Fig. 7). The extent of translation estimated from Figure 7 is of the order of 40–50°C as fluid saturation is approached (i.e. Crd<sub>HC</sub>+L+V). Hence, under conditions where CO<sub>2</sub>-rich cordierite is present, melting involving osumilite will only be seen in UHT granulites at >950–975°C. Cordierite in the sapphirine-bearing but osumilite-absent assemblages from Mount Sones and Mount Hardy in the Napier Complex (Table 1) contain 0.5 and 1.05 wt.% CO<sub>2</sub>, respectively, suggesting a role for CO<sub>2</sub> in stabilising cordierite with respect to osumilite, which does occur in other sapphirine-bearing Mg–pelites from these localities.

It is possible that the KFMASH [Bt] point, which is more completely denoted as [Bt, Spr] if sapphirine is considered as an additional UHT mineral, is rendered metastable in CO<sub>2</sub>-saturated conditions. This will occur if the displaced (Bt) KFMASH–C reaction involving Crd, Grt, Opx, Sil, Os, Qz and L translates up P and T to intersect the group of UHT reactions which involve Spr+Qz at 1040–1050°C (Bertrand *et al.* 1991; Audibert *et al.* 1995; Carrington & Harley 1995b; Harley 1998a). In this case, the (Bt, Crd, L) reaction of Figure 5b:



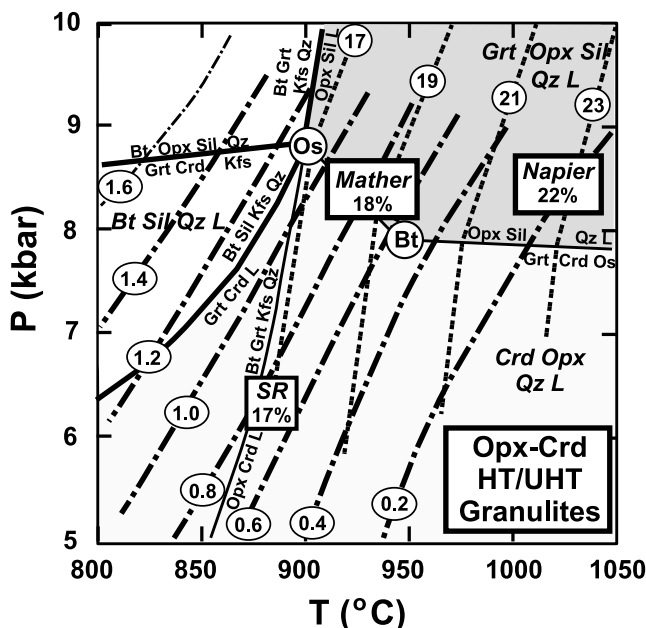
is reduced to zero length, and its high-T terminating invariant point [Bt, Crd, L] will be replaced by others, such as [Bt, Sil, L] and [Bt, Grt, L], which involve Spr+Opx+Os+Qz and CO<sub>2</sub>-rich (but H<sub>2</sub>O-bearing) cordierite. The linking KFMASH–C reaction:



will limit cordierite stability to high P–T. Therefore, cordierite with volatile contents of H<sub>2</sub>O <0.2 wt.% and CO<sub>2</sub> <1.8 wt.% could, in principle, coexist with all the other UHT phases in the absence of melt.

### 7. Integration with other UHT indicators: Opx–Crd relationships

Cordierite may coexist with orthopyroxene and melt over a wide range of HT/UHT conditions in rocks of appropriate



**Figure 8** Pressure–temperature (P–T) diagram illustrating the P–T conditions of equilibration of the Crd+Opx migmatites/granulites listed in Table 1. This diagram is contoured for the H<sub>2</sub>O contents of cordierite formed in equilibrium with KFMASH granitic melt (dashed lines with wt.% H<sub>2</sub>O indicated in ellipses), and for the Al<sub>2</sub>O<sub>3</sub> content of orthopyroxene as modelled by Kelsey *et al.* (2003) and expressed in terms of mol% MgTs component. The agreement between the measured cordierite H<sub>2</sub>O data and orthopyroxene MgTs contents is good in all three examples. Sources for P–T estimates are given in Table 1 along with the relevant cordierite compositional data; SR: Strangways Range.

bulk composition (Hensen & Green 1973; Carrington & Harley 1995a). At pressures less than those defined by the KFMASH [Os] and [Bt] points (Fig. 5a), relatively magnesian sub-aluminous to moderately aluminous pelites (i.e. compositions below the Grt–Crd tieline on an AFM diagram) may contain Crd+Opx+Qz+L at T>870°C. At higher pressures where the Opx+Sil+Qz+L sub-assemblage is stable, cordierite is restricted in FMAS and KFMASH to highly magnesian bulk compositions lacking garnet (e.g. Hensen 1971; Hensen & Green 1973; Bertrand *et al.* 1991; Carrington & Harley 1995a; Harley 1998a), but may be present along with garnet in slightly less magnesian bulk compositions ( $X_{Mg} > 0.65$ ) if the stabilising effect of CO<sub>2</sub> is considered. When garnet, sillimanite or sapphirine are present along with Opx+Crd, it is possible to estimate the temperatures of metamorphism using the Al<sub>2</sub>O<sub>3</sub> content of the orthopyroxene (Ganguly *et al.* 1996; Aranovich & Berman 1997; Harley 1998a, Hollis & Harley 2003; Kelsey *et al.* 2003), and compare such estimates with those inferred from the H<sub>2</sub>O contents of the cordierite. This comparison is illustrated for three examples of cordierite-bearing UHT assemblages in Figure 8.

Migmatitic Opx+Sil+Grt+Kfs ± Qz gneisses at Mather Peninsula in the Rauer Islands of East Antarctica have been described in detail by Harley (1998b). These contain magnesian garnet ( $X_{Mg} > 0.66$ ), aluminous orthopyroxene ( $X_{Mg}=0.78–0.82$ ; Al<sub>2</sub>O<sub>3</sub>=8.5–10 wt.% zoning up to 12% on rims) and sillimanite in palaeosomes/mesosomes. Similarly, magnesian garnets occur in 3–10-mm-thick leucosomes along with 2–8-mm-diameter subhedral aluminous orthopyroxene (Al<sub>2</sub>O<sub>3</sub>=9 wt.%) and microperthite. Locally, the leucosomes also contain cordierite ( $X_{Mg}=0.90$ ; H<sub>2</sub>O=0.7 wt.%; CO<sub>2</sub>=0.06 wt.%), in apparent textural equilibrium with the aluminous orthopyroxene and, by association, with the mesosome assemblage Grt+Opx+Sil. The P–T and  $a_{H_2O}$

conditions of extraction and crystallisation of the leucosomes can be assessed from the cordierite H<sub>2</sub>O contents by reference to Figure 8. This indicates P–T conditions of ca. 8.5 kbar and 925°C, and  $a_{H_2O}$  (Table 1) of  $0.09 \pm 0.01$ . In Figure 8, a set of calculated orthopyroxene Al<sub>2</sub>O<sub>3</sub> isopleths, expressed in terms of the mol% MgTs (Mg-tschermaks) component, are superimposed on the cordierite H<sub>2</sub>O isopleths so that the P–T conditions defined above can be independently assessed. These Al<sub>2</sub>O<sub>3</sub> isopleths (Kelsey *et al.* 2003), calculated for the assemblages Grt+Opx+Sil+Qz+L and Grt+Crd+Opx+Qz+L, are in reasonable agreement with those presented by Harley (1998a); over the temperature interval 910°C<T<1050°C, MgTs varies from 17 to 23 mol% in the modelled isopleth set of Kelsey *et al.* (2003), whereas MgTs ranges from 16 to 25 mol% in the Harley (1998a) isopleth diagram. It is encouraging that the MgTs isopleths, cordierite H<sub>2</sub>O isopleths and assemblage constraints all match rather well. This suggests that, at least in the present case study, the cordierite has preserved its UHT volatile contents. This is interpreted to reflect melt loss from the Mather Peninsula migmatitic gneiss leucosomes (e.g. Kriegsman 2001; Kelsey *et al.* 2003), which are residual or in their overall chemistry and preserve anhydrous mineral assemblages only partially retrogressed to biotite-bearing ones (Harley 1998b). Melt loss early in the UHT history, and certainly below the peak conditions attained by these rocks (ca. 11–12 kbar, 1030°C; Harley 1998b), is interpreted to have enabled the preservation of the prograde melting record since the leucosomes acted as closed systems following the loss of hydrous melt components.

Grt+Crd+Opx+K-feldspar leucosomes occur as local patchy segregations in semipelitic gneisses near Phlogopite Mine in the Strangways Ranges, which comprise part of the Arunta Complex of central Australia. Cordierite H<sub>2</sub>O contents (Table 1) are consistent with dehydration melting via Reaction R3 at 875–900°C if pressures were 6–7 kbar. The orthopyroxene in these leucosome patches contains 7.7 wt.% Al<sub>2</sub>O<sub>3</sub>, or 17 mol% MgTs, once again consistent with the temperatures implied by the cordierite H<sub>2</sub>O data, and therefore, suggestive of melt loss at these conditions, followed by an absence of any fluid that could interact with and hence change the H<sub>2</sub>O content of the preserved cordierites.

The final comparison of cordierite H<sub>2</sub>O content with the Al<sub>2</sub>O<sub>3</sub> contents of orthopyroxene in the same UHT assemblage is provided by the sapphirine+orthopyroxene+quartz granulite from Mount Hardy, East Antarctica (Table 1). This granulite occurs in the UHT sapphirine+quartz zone of the Archaean Napier Complex (Ellis *et al.* 1980; Sheraton *et al.* 1987; Harley & Hensen 1990) and is inferred to have experienced P–T conditions in the region of 8–9 kbar and greater than 1000°C (Harley & Hensen 1990), with even higher temperatures (>1120°C) possible on the basis of comparisons with a sapphirine+orthopyroxene+quartz granulite reported from Mount Riiser-Larsen nearby (Harley & Motoyoshi 2000). Cordierite not only occurs in the Mount Hardy sample as coronas on sapphirine+quartz, but also as large grains in apparent textural equilibrium with orthopyroxene rims which contain up to 10–11 wt.% Al<sub>2</sub>O<sub>3</sub>, or 22 mol% MgTs. Figure 8 demonstrates that the measured H<sub>2</sub>O content of this cordierite (0.22 wt.%) is consistent with the P–T conditions inferred from the orthopyroxene, and is suggestive of the presence of some melt that may have back-reacted with the UHT assemblage to produce this cordierite. Although the CO<sub>2</sub> content of the cordierite is significant (1.04 wt.%), it is not high enough to saturate the cordierite at these P–T conditions, or indeed, any P–T conditions along the post-peak IBC path experienced by the Napier Complex. Hence, in this case, the present authors suggest that the cordierite formed in the absence of a free

fluid phase, under low  $a_{\text{H}_2\text{O}}$  (ca. 0.03) and high  $a_{\text{CO}_2}$  (0.58) conditions mediated by the presence of a small amount of melt.

## 8. Conclusions

As emphasised in many previous studies (e.g. Hensen 1971; Hensen & Green 1973; Aranovich & Podlesskii 1989; Vry *et al.* 1990; Bertrand *et al.* 1991; Audibert *et al.* 1995; Carrington & Harley 1995a, b; Fitzsimons 1996; Harley 1998a; White *et al.* 2001; Harley *et al.* 2002), cordierite plays a significant role in the high-grade metamorphism and anatexis of pelites. The P–T-dependent  $\text{H}_2\text{O}$  exchange equilibrium between cordierite and granitic melt exerts a strong control on melt production from such rocks. Moreover, the variable  $\text{CO}_2$  contents of cordierite formed coexisting with melt influences the P–T positions of melting reactions, expanding the stability fields of cordierite+melt assemblages in KFMASH- $\text{CO}_2$  at the expense of UHT indicator assemblages such as orthopyroxene+sillimanite+K-feldspar+quartz and osumilite+garnet.

SIMS microanalysis of natural cordierites from a selection of HT/UHT migmatitic and granulite terrains yields  $\text{H}_2\text{O}$  contents which are consistent with cordierite-melt equilibrium at temperatures  $>860^\circ\text{C}$ , and in most cases, in agreement with calculated KFMASH grids and independent equilibria, irrespective of the  $\text{CO}_2$  contents of the cordierites. This gives confidence that volatiles in cordierite, analysed carefully, and with sufficient spatial resolution to evaluate and volatile zoning or leakage, can provide valuable information on the fluid and melting conditions attending HT/UHT metamorphism. With the notable exception of the Calabrian granulites, which appear to have been fluid-saturated at HT conditions and equilibrated in the presence of a  $\text{CO}_2$ -rich fluid phase at or near peak metamorphic conditions, cordierites from the migmatitic granulites studied thus far yield  $\text{CO}_2$  and  $\text{H}_2\text{O}$  contents which produce calculated  $a_{\text{CO}_2}$  and  $a_{\text{H}_2\text{O}}$  which sum to less than unity. These imply metamorphism under fluid-absent conditions, but in the presence of melts which contain 1.3–2.5 wt.%  $\text{H}_2\text{O}$  and, in many cases, appreciable dissolved  $\text{CO}_2$ . It is clear that the volatile contents of cordierite in HT/UHT metamorphic and magmatic rocks cannot be assumed to adhere to saturation values or ignored in calculations of mineral and mineral-melt equilibria: they must be routinely measured and incorporated into the assessment and analysis of the P–T and P–T–X-fluid evolution of high-grade terrains.

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