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The distribution of H_2O–CO_2 between cordierite and granitic melt under fluid-saturated conditions at 5 kbar and 900 °C

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Abstract Experiments to determine the distribution of H_2O and CO_2 between synthetic peraluminous granitic melt and natural Fe–Mg cordierite have been conducted at 5 kbar and 900 °C under fluid-saturated conditions. Up to seven charges, saturated with a range of H_2O–CO_2 fluid compositions, were run simultaneously. The H_2O and CO_2 contents of the cordierites and the H_2O contents of the melts were determined using secondary ion mass spectrometry. As the CO_2 content of the fluid increases, the H_2O content of both the cordierite and the melt decrease in a similar manner to fluid-undersaturated experiments in the H_2O only system. The cordierite H_2O contents in the experiments range from 0.5 to 1.7 wt% H_2O. The distribution coefficients ($Dw = \text{wt\% } H_2O^{(melt)}/\text{wt\% } H_2O^{(cordierite)}$) are in the range 3.5–5.9 and agree with the model of Harley and Carrington for 5 kbar and 900 °C. The CO_2 content of the cordierite increases from 0 to 1 wt% CO_2 in the most CO_2-rich experiment as the cordierite and melt H_2O contents decrease. Our H_2O–CO_2 cordierite data allow us to model and predict the maximum CO_2 content in cordierite to be 0.16 ± 0.01 molecules per formula unit (i.e. 1.16 wt% CO_2) at 5 kbar and 900 °C. This value, and the channel CO_2 contents of cordierite in equilibrium with H_2O–CO_2 fluids at high XCO_2, are significantly lower than predicted using previous models. On the basis of these experiments cordierites that are saturated in $H_2O + CO_2$ and have channel $XCO_2 > 0.25$ require aCO_2 of over 0.75.

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Introduction

It is widely recognised that fluids and melts play important roles in the formation and evolution of mineral assemblages during and following high-grade metamorphism in the deep crust. The formation of granulites, migmatites and granites in high-grade terranes may reflect the relative significance of fluid infiltration (e.g. Newton et al. 1980; Santosh et al. 1990; Schmulovich and Graham 1996) compared with melt-present but fluid-absent conditions during metamorphism (Waters and Whales 1984; Barbey et al. 1990; Stevens and Clemens 1993; Watt and Harley 1993) and, as a consequence, it is essential to constrain and elucidate the fluid regime of high-grade metamorphism using a range of complementary approaches.

In order to discriminate fluid-present from fluid-deficient (and often melt-present) conditions, mineral monitors of fluid conditions are required that can complement the isotopic, reaction-progress and mineral equilibria approaches commonly employed to evaluate the extents of fluid interaction and activities of fluid species. Cordierite, $(Mg, Fe)_2Al_4Si_5O_{18}.(nH_2O, mCO_2)$, is potentially a powerful mineral monitor as it incorporates both H_2O and CO_2 within its channel structure and hence can constrain H_2O and CO_2 contents in any coexisting fluid or melt (Goldman et al. 1977; Armbruster and Bloss 1980, 1982; Johannes and Schreyer 1981; Kurepin 1984; Schreyer 1985; Vry et al. 1990). In fluid-present metamorphic environments the absolute abundance and XCO_2 $[= CO_2/(CO_2 + H_2O)]$ of channel volatiles in cordierite depends on pressure, temperature and XCO_2 in the coexisting fluid (Johannes and Schreyer 1981; Armbruster and Bloss 1982). However, in environments where a free volatile phase is not present but temperatures are high (> 750–800 °C; e.g. Vielzeuf and Holloway 1988), the absolute abundance of these channel volatiles may instead depend upon partitioning of H_2O and CO_2 between the cordierite and melt (Harley 1994; Stevens et al. 1995; Carrington and Harley 1996).

Characterisation of the channel volatiles in cordierite formed under known P–T conditions therefore has the potential to discriminate between fluid-present, fluid-absent and melt-present conditions and allow estimation of fluid activities in metamorphism.

The objective of the present experimental study is to determine how the H_2O and CO_2 contents of cordierite vary with the volatile composition of the coexisting fluids and/or melts at 5 kbar and 900 °C. The results define the hitherto poorly-constrained cordierite volatile saturation surface (Johannes and Schreyer 1981; Kurepin 1984; Vry et al. 1990) and demonstrate that the previous modelling of volatile saturation data requires major modification. The saturation data obtained enable cordierite to be used as a monitor of the water contents of the melts that were present during crustal anatexis, as an indicator of the H_2O–CO_2 compositions of fluids that interacted with rocks during their metamorphism, and as a sensor of fluid activities.

Existing data on H_2O–CO_2 contents of cordierite and melts

Volatile contents in cordierite

The maximum volatile contents of cordierite coexisting with pure H_2O have been experimentally calibrated and modelled over the P–T range 1–9 kbar 500–1,000 °C by Harley and Carrington (2001) based on their experiments on Fe–Mg cordierite at 800–1,000 °C and previous experiments on Mg-, Fe- and Fe–Mg cordierite at lower-T (Mirwald and Schreyer 1977; Mirwald et al. 1979; Boberski and Schreyer 1990; Mukhopadhyay and Holdaway 1994; Carey 1995; Skippen and Gunter 1996). Maximum H_2O channel occupancies fit a one-site model (Harley and Carrington 2001) that is compatible with the internally-consistent data set of Holland and Powell (1998).

The situation for the H_2O–CO_2 system is far more uncertain. Experimental data by Johannes and Schreyer (1981) and Armbruster and Bloss (1982) define maximum volatile contents (i.e. the saturation surface of Mg-cordierite in the presence of H_2O–CO_2 and CO_2 respectively) that are mutually inconsistent. Johannes and Schreyer (1981) found that CO_2 contents at 5 kbar and 600 °C differed significantly between different synthetic starting materials, possibly dependent upon the presence of alkali cations in the channels (Johannes and Schreyer 1981; Schreyer 1985). Their cordierite A, an alkali-free synthetic cordierite, showed a trend of increasing CO_2 content that was scattered at higher $CO_2/CO_2 + H_2O$ ratios. Johannes and Schreyer (1981) also presented the results for another synthetic cordierite (B) that showed considerably lower CO_2 contents for a specified fluid composition, but with a much less scattered trend. The CO_2 content in the H_2O-free system determined by Armbruster and Bloss (1982) at equivalent pressures was very high even by comparison with the trend from cordierite A of Johannes and Schreyer (1981).

The effects of P, T and XCO_2 on cordierite volatile contents have been modelled (Vry et al. 1990) to produce saturation surfaces which are the basis for comparison of analytical data on natural cordierites with predictions from experiments. This saturation surface modelling is, however, simplistic and largely based on the cordierite A volatile content data obtained by Johannes and Schreyer (1981) coupled with the CO_2-system result of Armbruster and Bloss (1982). Kurepin (1984) modelled the saturation surfaces of H_2O–CO_2 fluids in cordierite at polybaric and polythermal conditions assuming a one-site model with a fit to the H_2O solubility data from the water-only system (Mirwald et al. 1979) and a model of H_2O–CO_2 behaviour in cordierite that approximates the cordierite A data of Johannes and Schreyer (1981). Cordierite B fitted this model at lower pressures and higher water contents at 600 °C but otherwise the CO_2 contents were significantly lower than those predicted by the Kurepin (1984) model. The fit of both the cordierite A and B data also appear to deteriorate at the temperature extremes, but nevertheless the Kurepin (1984) model has been used extensively in later applications and is applied in the internally-consistent data set approach of Holland and Powell (1998) despite its shortcomings.

Further attempts at defining the saturation contents of CO_2 in cordierite in the H_2O-free system have been largely unsuccessful, and moreover have failed to duplicate the early result of Armbruster and Bloss (1982). Le Breton and Schreyer (1993) could not equilibrate natural and synthetic cordierites with CO_2 fluid in their experiments carried out at 8–12 kbar and 600–800 °C in piston cylinder (solid media) apparatus. These workers found that CO_2 contents varied with experimental run duration, and in particular documented oscillations in CO_2 with time. There is no completely satisfactory explanation of this behaviour.

In this study we adopted a three-phase experimental design to minimise problems of volatile equilibration in cordierite. Each experiment contains cordierite, melt and a coexisting H_2O–CO_2 fluid phase. H_2O is strongly incorporated into the melt and cordierite and the fluid XCO_2 can be varied to high values at specified P–T conditions. The presence of melt with cordierite provides limits on post-run volatile adjustments in cordierite as melt–cordierite contacts become 'locked' at the quench temperature of the melt. Moreover, both cordierite and melt can be used as monitors of the H_2O activity of the experiment (Harley and Carrington 2001) and hence the approach to equilibrium.

Volatiles in felsic and peraluminous melts

The maximum solubilities of H_2O in eutectic melts within various simplified granitic systems are now well-defined from several studies (e.g. Holtz et al. 1992; Holtz

and Johannes 1994; Papale 1997). The maximum solubility of CO_2 in rhyolitic melts, although low at mid-crustal pressures (< 4,000 ppm) is strongly pressure-sensitive (Fogel and Rutherford 1990; Blank and Brooker 1994; Holloway and Blank 1994). In contrast to the large database now available for H_2O, the combined solubilities of H_2O and CO_2 in felsic melts in a mixed volatile system are poorly known at pressures greater than 2 kbar, even though such pressure conditions (2–8 kbar) are highly relevant to the generation and segregation of many crustally-derived magmas. The present study also explores the variation in the H_2O content of a granitic melt with differing fluid compositions at 5 kbar and 900 °C. The variation in melt CO_2 contents were too small to detect with appropriate levels of precision using secondary ion mass spectrometry, but the small quantity of CO_2 (probably < 1,000 ppm) can be demonstrated to have negligible effect on the behaviour of H_2O in the melt.

Experimental design

The presence of a melt along with cordierite and fluid has three advantages compared with simple experiments that attempt to equilibrate cordierite with only a mixed H_2O–CO_2 fluid phase:

1. The melt provides a reservoir for H_2O that effectively 'quenches in' at high temperatures (> 650–750° C) and hence causes the experiment to 'lock-in' soon after power is cut off. This limits the opportunity for low-temperature Crd–fluid exchange, which could modify the cordierite H_2O–CO_2 contents from those of the run conditions, to progress at intact cordierite–melt contacts. There are very few fluid bubbles present at Crd–melt contacts in these experiments, so that a large fluid reservoir is not available to exchange with the cordierite once the melt has solidified.
2. The approach to equilibrium can be judged, at least for H_2O contents, by comparing measured distribution coefficients (Dw = wt% $H_2O^{(melt)}$/wt% $H_2O^{(cordierite)}$) with those predicted from the models of Harley and Carrington (2001) in the H_2O-only system, governed by equilibria (1) and (4) below.
3. aH_2O (and from this, aCO_2) can be calculated from both cordierite and melt, albeit with differing uncertainty limits depending on the homogeneity of the run products. Hence, in experiments where the cordierite H_2O data are subject to high relative analytical errors, the melt H_2O data can provide more precise aH_2O estimates for defining the relations between aCO_2 and $XCO_{2(Crd)}$.

Experimental charges comprised cordierite (Crd), granitic melt (L) and an H_2O–CO_2 fluid (V). In this system the following equilibrium relationships describe the uptake of H_2O and CO_2 in cordierite:

$$A - \mathrm{Crd} + H_2O = H - \mathrm{Crd} \quad (1)$$

and

$$A - \mathrm{Crd} + CO_2 = C - \mathrm{Crd} \quad (2)$$

which are linked by the exchange relationship:

$$H - \mathrm{Crd} + CO_2 = C - \mathrm{Crd} + H_2O \quad (3)$$

where A-Crd is volatile-free cordierite, H-Crd is hydrous cordierite (Crd.H_2O, with H_2O up to a maximum of one molecule per formula unit of cordierite) and C-Crd is Crd.CO_2, with CO_2 up to a maximum of one molecule per formula unit.

Furthermore, exchange equilibria for H_2O and CO_2 apply between the cordierite and granitic melt:

$$A - \mathrm{Crd} + H - \mathrm{melt} = H - \mathrm{Crd} + A - \mathrm{melt} \quad (4)$$

and

$$A - \mathrm{Crd} + C - \mathrm{melt} = C - \mathrm{Crd} + A - \mathrm{melt} \quad (5)$$

As demonstrated in previous studies in the H_2O-only subsystem, the Fe–Mg composition of cordierite does not have a measurable effect on the molecules per formula unit of volatile incorporated in the phase at a given P–T and aH_2O (Boberski and Schreyer 1990; Carrington and Harley 1996; Harley and Carrington 2001). A natural cordierite, BB3a, with $X_{Mg} = 0.66$ (Table 1) was used once it had been crushed and sieved to 125–250 μm. This cordierite had been evacuated of all volatiles prior to the experiment by prolonged step-heating in a high vacuum at temperatures of up to 1,200 °C. In this evacuation procedure the cordierite is held for 1 h at each 100 °C temperature step below 1,200 °C, for 2 h at 1,200 °C, and heated for a minimum of 12 h in total. The vast proportion of CO_2 is liberated from the cordierite channels only at temperatures over 800 °C, and often at above 1,000 °C. The granitic melt was introduced into the experiments in the form of a K_2O–Na_2O–FeO–MgO–Al_2O_3–SiO_2 system gel ($X_{Mg} = 0.25$, Table 1) and chosen to be close to Fe/Mg equilibrium with the cordierite (Carrington and Harley 1995). Different fluid compositions were generated in different charges by adding carefully measured quantities of distilled H_2O (using a microsyringe), silver oxalate ($Ag_2C_2O_4$ decomposes to release 29.0 wt% CO_2) and oxalic acid [$(COOH)_2.2H_2O$ decomposes to release 69.8 wt% CO_2 and 28.6 wt% H_2O]. Table 2 gives the proportions of starting materials in each run. The experiments were performed at 5 kbar and 900 °C in an internally heated gas apparatus that has pressure and temperature uncertainties of ± 0.2 kbar and ± 5 °C, respectively (Carrington and Harley 1995). Up to seven charges with differing fluid compositions could be run in one operation for between 137 and 524 h. Tantalum chips were placed outside the capsules to moderate the f_{O_2} and prevent loss of hydrogen from the capsule fluids. At the end of the experiment the charges were weighed, pierced

Table 1 Experimental starting materials and SIMS standards: mean electron microprobe analyses ($n = 6$). Melt data has been normalised to ease comparison

	Starting materials	Standards		
	BB3a	81–90	AMNH	
SiO_2	48.12	47.70	48.70	
Al_2O_3	33.02	32.72	33.16	
FeO	8.61	6.19	2.58	
MgO	8.57	9.74	12.24	
K_2O	0.03	0.11	0.39	
Na_2O	0.05	0.01	0.01	
H_2O[a]		0.80	1.54	
CO_2		1.3[b]	0.7[c]	
Total	98.42	97.29	98.63	
X_{Mg}	0.64	0.74	0.89	
	Melt gel	Glass standards		
SiO_2	73.57	74.46	75.78	76.43
Al_2O_3	15.05	16.46	15.89	15.94
FeO	1.82	0.70	0.59	0.72
MgO	0.40	0.15	0.13	0.14
K_2O	4.79	3.36	2.66	1.94
Na_2O	4.37	4.26	4.35	4.24
H_2O[d]		2.1	3.9	5.6
Total	100.00	100.00	100.00	100.00
X_{Mg}	0.28	0.28	0.28	0.25

[a]By hydrogen extraction and manometry (A. Fallick)
[b]By coulometric titration (V. Schenk)
[c]By stepped-heating mass spectrometry (D. Mattey)
[e]Karl–Fisher titration (F. Holtz)

Table 2 Starting materials, run durations and SIMS analyses of the H_2O and CO_2 contents of cordierites and melts for all experiments used in this study. SIMS errors given in brackets are 1σ values propagated from variations in the analysis populations ($n = 8$–10). No data = not included in charge

	Starting materials						Experimental results		
	H_2O (g)	Oxalic acid (g)	Silver oxalate (g)	Cordierite (g)	Melt gel (g)	Time (h)	Cordierite wt% H_2O	Cordierite wt% CO_2	Melt wt% H_2O
C13-1 (–)	2.84	–	2.51	3.02	7.08	137	2.03 (0.09)	0.26 (0.05)	8.57 (0.37)
C13-2 (–)	2.21	–	4.16	2.48	7.15	137	1.73 (0.08)	0.29 (0.01)	8.23 (0.82)
C13-3 (–)	1.52	–	5.06	2.25	6.93	137	1.59 (0.07)	0.44 (0.04)	6.97 (0.54)
C13-4 (–)	–	3.94	3.89	2.83	7.11	144	1.33 (0.07)	0.64 (0.07)	5.49 (0.28)
C13-5 (–)	–	2.03	5.13	3.01	7.86	144	1.09 (0.07)	0.80 (0.06)	3.86 (0.28)
C19-4 (–)	0.30	–	2.44	2.78	6.48	238	0.57 (0.03)	1.01 (0.14)	Crystallised
C19-3b (–)	0.33	–	2.18	2.66	6.61	524	0.64 (0.08)	1.03 (0.17)	Crystallised
C20-1 (–)	0.45	–	2.08	2.56	5.61	173	1.37 (0.14)	0.53 (0.05)	6.03 (0.68)
C13-1 (+)	2.84	–	2.51	3.02	7.08	137	1.55 (0.07)	0.26 (0.05)	8.57 (0.37)
C13-5 (+)	–	2.03	5.13	3.01	7.86	144	0.92 (0.04)	0.80 (0.06)	3.86 (0.28)
MP13B (+)[a]	1.28	–	–	2.56	6.56	311	1.70 (0.05)	0.00 (0.00)	10.02 (0.42)
H_2O model[a]							1.76	0.00	10.20

[a]Data from Harley and Carrington (2001)

and reweighed to check for capsule integrity during the experiment. They were then vacuum impregnated with epoxy resin, mounted and polished until a section through the cordierite grains and melt was observed.

Characterisation and analysis of run products

Initially, the polished charges were examined optically for the presence of fluid inclusions in the melt. Fluid-saturated experiments contain a free fluid during the experiment that may be trapped as bubbles in the melt on quenching. Cordierite and melt were the only run products in most cases, but at low H_2O contents (< 2.2 wt% H_2O) the melts partially or completely crystallised to quartz and feldspar, as is expected from their near-eutectic compositions. In the two most H_2O-rich experiments cordierite showed minor resorption producing fine grains of spinel located at cordierite–melt contacts.

The H_2O and CO_2 contents of the experimental cordierite and melt were analysed using secondary ion mass spectrometry (SIMS). All other oxides were measured with a wavelength-dispersive electron microprobe (EMP) in Edinburgh and compared with data from the energy-dispersive scanning electron microscope (SEM) using a cold stage in Manchester. The analytical conditions used for EMP were the same as those detailed in

Carrington and Harley (1996) and Harley and Carrington (2001). Calibration curves were obtained in each SIMS session by analysis of melts and cordierites of appropriate compositions, but differing volatile contents that had been independently determined (Table 1) The three melt standards contained 2.1, 3.9 and 5.6 wt% H_2O (provided by Dr F.R. Holtz). Melts with higher H_2O contents (up to 10 wt%, the approximate saturation content at 5 kbar and 900 °C) were synthesised, but were unstable over long time periods at room pressure and temperature. The two cordierite standards contained 1.56 (AMNH) and 0.86 (81/90) wt% H_2O and 0.66 (AMNH) and 1.30 (81/90) wt% CO_2, respectively. All melt analyses and a subset of the cordierite analyses were obtained using an O^- primary beam (8 nA, 10 kV) and by measuring positive secondary ions (H^+, ^{30}Si) at an energy offset of 75 V. Cordierites were also analysed using negative secondary ions (H^-, ^{12}C and ^{28}Si) at an energy offset of 60 V. The sputtered pit in the sample is roughly 25 μm in diameter in the positive mode and 35 μm in the negative mode. Each analysis involves a 3-min burn-in time followed by 30 cycles of 5-s counts for each isotope. The mean of the isotope ratios of the last 10 cycles was taken as the final result, thereby avoiding surface contamination. Analyses were expressed as isotopic ratios of $H^+/^{30}Si$ (positive mode) or $H^-/^{28}Si$ and $^{12}C/^{28}Si$ (negative mode) and then converted to wt% H_2O or CO_2 by comparison with the calibration lines from the standards from the same analytical session. Standard errors on analytical populations for individual standard melt and cordierite grains with positive secondary ions were typically ± 0.8 and ± 0.2 wt% H_2O, respectively, yielding calibration curves with 2 sigma uncertainties of 0.15 and 0.06 wt% H_2O for melt and cordierite H_2O contents of 3 and 1 wt% H_2O, respectively. Equivalent standard errors on analytical populations for individual standard cordierite grains measured with negative secondary ions were ± 0.16 wt% H_2O and ± 0.08 wt% CO_2. Calibration curves for negative secondary ions thus had 2 sigma uncertainties of 0.12 wt% H_2O and 0.06 wt% CO_2 for 1 wt% H_2O and 1 wt% CO_2 in the cordierite. respectively.

Difficulties were encountered in measuring the low CO_2 contents (< 1,000 ppm) in melt standards and hence also in the experimental granitic melts, which appear to contain less than 1,000 ppm CO_2, that form in equilibrium with cordierite of moderate CO_2 content (< 1 wt%) and are significantly lower than the maximum CO_2 contents (~2,600 ppm) in rhyolite glass at 900 °C (Holloway and Blank 1994). The glass standards were mounted in indium metal to minimise the carbon background resulting from any epoxy resin. Despite this, the measured $^{12}C/^{28}Si$ ratios for glasses synthesised nominally without CO_2 were indistinguishable from those measured for a glass characterised by FTIR spectroscopy (Bristol) to have 300 ppm CO_2. To further reduce the presumed high carbon background, a 50-nA primary beam was rastered over 50 μm and the counts measured through a 10-μm aperture, but the sum of the counts from background carbon and from any CO_2 in the 'blank' glasses was still at least 300 ppm. In view of these problems we concentrated on obtaining H_2O analyses on the melts (positive mode) and H_2O–CO_2 on the cordierites (negative mode CO_2; positive and negative mode for H_2O).

Experimental results

Phase chemistry

Melts

The melt composition was chosen to be in Fe/Mg equilibrium with the cordierite and close to the eutectic minimum melt composition (Carrington and Harley 1996). The oxide contents of the final experimental glasses were analysed using the electron microprobe. The lack of a cold stage on the electron microprobe caused significant volatilisation of the sodium. These 5 kbar, 900 °C samples were all mounted in indium and could not be thinned for analysis on the analytical SEM cold stage in Manchester. However, the data could be corrected for sodium loss by comparison with both EMP and SEM data from similar experiments at other pressure–temperature conditions. These comparisons indicate that the glasses did not change significantly from the minimum melt composition in any of the experiments and were in close agreement with the data for the water-undersaturated system of Harley and Carrington (2001). Thus the presence of CO_2 in the system, and hence in the melt, does not appear to change the melt compositions significantly. This is important in respect of controversy regarding the stabilisation of lamprophyric melt compositions in felsic systems, as proposed by Petersen and Newton (1990) and disputed by Clemens (1993) and others. Our results reconfirm the conclusions of Clemens (1993) that CO_2 does not enhance melting and certainly does not shift melt compositions to high-K, low-Si compositions.

Cordierites

Product cordierite compositions demonstrate the same effects as that seen in the H_2O experiments of Harley and Carrington (2001). Occasionally some cordierites showed minor near-rim shifts in X_{Mg}, usually to slightly higher X_{Mg} as indicated by back scattered electron brightness changes. Apart from these rims, systematic analyses of cordierite compositions are very consistent. Only potassium varies, by less than 0.2 wt% K_2O. The potassium content increases with temperature and decreases with water content, as reported in Thompson et al. (2001).

Fluids

All experiments contained a free fluid phase during the run, as shown by capsules emitting gas when pierced and

by weight loss. Polished surfaces showed sections through bubbles in the melt phase. These fluids were not analysed after the experiments. The initial proportions in Table 2 can be used to calculate the initial fluid composition and estimate the final fluid compositions by mass balance. However, such estimates may involve several sources of error and hence are less reliable for activity calculations than the methods we use below. Potentially important sources of error include inaccuracies in capsule manufacture, small changes in the proportions of the phases during the experiments (e.g. because of reaction) and cumulative uncertainties on the measured volatile contents of the phases. The unquantified CO_2 contents of the experimental melts have a negligible effect on the mass balance calculations; a maximum CO_2 content of 2,600 ppm (Holloway and Blank 1994) would only change our fluid XCO_2 estimates by less than 0.2%. Our mass balance calculations (not tabulated) are generally consistent with the estimates of fluid XCO_2 produced using the approach adopted here (see later section). However, as they show significantly greater scatter in estimated XCO_2 they are not used in further calculations.

Time study – approach to equilibrium

In the H_2O experiments at 5 kbar and 900 °C of Harley and Carrington (2001) sandwich-type charges showed that the values of D_w [= wt% $H_2O^{(melt)}$/wt% $H_2O^{(cordierite)}$] of initially evacuated cordierite at one end and fully saturated cordierite at the other approached each other with 24 h. The presence of CO_2 may affect the diffusion of volatiles in the cordierite and hence a time study was conducted to evaluate the approach to equilibrium in CO_2-rich compositions. Four charges were made with similar bulk initial proportions of 2.9 ± 0.3 wt% H_2O, 6.5 ± 0.4 wt% CO_2, 25.6 ± 1.5 wt% evacuated cordierite and 64.9 ± 1.8 wt% gel. These four charges were then run for different durations. The final compositions of these experiments are shown in Table 3. After 119 h, the volatile compositions of the cordierites agree within error implying that equilibrium of the cordierite volatile composition has been achieved. Equilibrium conditions are thus likely to have occurred in all further experiments that were run for 137–422 h.

Water contents of melts and cordierites

The results of SIMS analyses of the run products of all the H_2O–CO_2 data are listed in Table 2. Figure 1 is a plot of wt% of volatiles (H_2O or CO_2) in the cordierite against the wt% of H_2O in the melt from the same experiment. The H_2O contents in both the cordierite and melt decrease from their maximum values (1.78 and 10.20 wt% H_2O respectively in the pure water system) as the CO_2 in the cordierite increases.

The H_2O in the cordierites in two of the run products (C13-1 and C13-5) were measured with both positive (Fig. 1, open squares) and negative (Fig. 1, closed squares) secondary ions but all others were measured in negative mode alone. In our larger data set of cordierite–melt experiments, run over a range of P–T conditions, we have made 22 positive/negative comparisons. Of these 17 showed very close agreement between the values in both modes. However, two showed a slightly higher value in positives and two, C13-1 and C13-5 reported here, had significantly lower values in positives than negatives. C13-1, the most hydrous of the H_2O–CO_2 experiments, has a large difference between the cordierite water content measured in positive and negative mode. C13-5 shows that the difference is small at lower water contents. SIMS analyses of natural cordierites have also been compared in positives and negatives and no such sizeable discrepancies have been found. The reason for these occasional differences is not apparent, but in the light of all other experiments the values measured in positives appear more consistent and thus these are preferred in those cases where +/– discrepancies were

Table 3 Results of a time study to determine how long it takes to reach constant volatile content in cordierite with a CO_2-rich fluid. Starting materials are given in Tables 1 and 2

Run	Duration (h)	Cordierite (wt% H_2O)	Cordierite (wt% CO_2)	XCO_2 in Crd Channels
c19-1	24	0.84 (0.08)	0.88 (0.11)	0.30 (0.05)
c19-2	119	0.54 (0.03)	1.21 (0.16)	0.48 (0.08)
c19-4	238	0.57 (0.03)	1.01 (0.14)	0.42 (0.07)
c19-3b	524	0.64 (0.08)	1.03 (0.17)	0.40 (0.08)

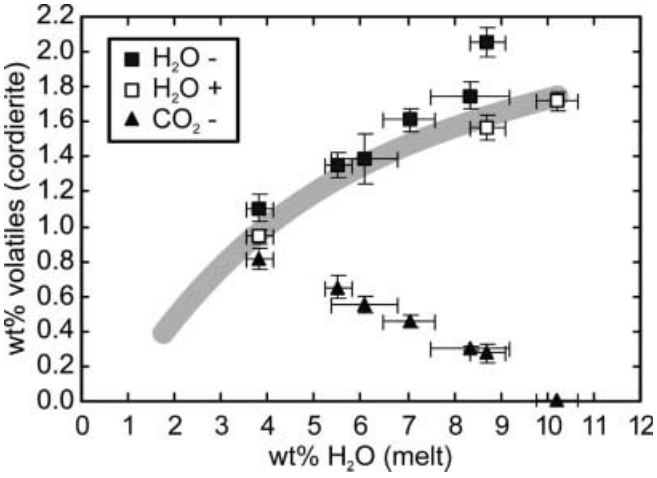

Fig. 1 A graph showing the volatile contents in the cordierite at 5 kbar, 900 °C as a function of the water content of the melt. *Squares* H_2O contents; *triangles* CO_2 contents; *closed symbols* H_2O measured in negative mode; *open symbols* H_2O contents measured in positive mode. The *thick line* is the trend of H_2O content (including errors) taken from Harley and Carrington (2001) for undersaturation in the water-only system. This trend reaches saturation at 1.76 and 10.20 wt% H_2O for cordierite and melt, respectively

found. The anomalous values in negatives may be a problem associated with that particular analysis session and thus all the other cordierite H_2O values for C13 may be slightly high.

The decrease in H_2O content of the cordierite with decreasing melt water content (Fig. 1) in these CO_2-bearing fluid-saturated experiments closely follows the behaviour of H_2O-undersaturated cordierites observed by Carrington and Harley (1996). Only C13-1 measured in negatives has an anomalously high value. The points measured in negatives all lie within error but on the high side of the trend shown by the water-only data whereas those in positive mode lie on the low side. Overall, the H_2O–CO_2 trend brackets and is indistinguishable within error from the H_2O-undersaturated trend defined by Harley and Carrington (2001), which is shown as a broad curve on Fig. 1.

The distribution coefficient [D_w = wt% $H_2O^{(melt)}$/wt% $H_2O^{(cordierite)}$] of H_2O between melt and cordierite is plotted in Fig. 2. The broad curve in Fig. 2 is taken from the model of the water-only system of Harley and Carrington (2001) for 5 kbar and 900 °C. The D_w values for the positive data and all negative data except the anomalous C13-1 (in negative mode) lie within error of this modelled trend. Therefore, the incorporation of CO_2 into cordierite and melt has no additional effect on D_w compared with the simple effect of reduction in aH_2O. For a melt of specified H_2O content D_w is the same whether the coexisting cordierite contains CO_2 or not.

Relation of CO_2 to water in cordierite

Figure 1 also shows the variation in the CO_2 content of the cordierite. The data all lie on a curve antithetic to the curve shown by the variation of the water content in the cordierite. The CO_2 contents range from zero in the hydrous cordierite to 0.8 wt% in the most CO_2-rich experiment of Fig. 2 where the melt is 3.86 wt% H_2O. It is possible to get higher cordierite CO_2 contents, of over 1 wt% CO_2, in experiments C19-4 and C19-3b, but at these conditions the water content of the melt drops below its minimum value [approximately 2 wt% H_2O, Johannes and Holtz (1996) and Carrington and Harley (1996)] and crystallises. The curve of Fig. 2 extrapolates to the CO_2-only end at a maximum value of CO_2 in cordierite of 1.16 wt% CO_2, a value derived by modelling of the data in terms of fluid activities (see below). Under these H_2O-free conditions melt is not stable at 900 °C.

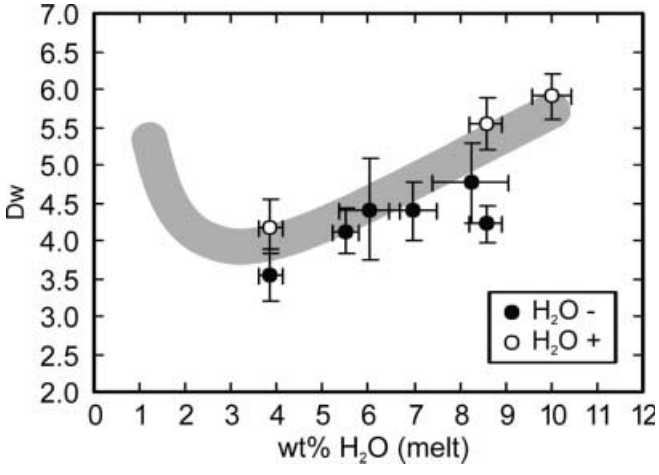

Fig. 2 The relation between the distribution coefficient D_w = [wt% $H_2O^{(melt)}$/wt% $H_2O^{(cordierite)}$] and the water content of the melt. *Closed symbols* Measured in negatives; *open symbols* measured in positives. The *thick line* shows the model (including errors) of D_w variation with undersaturation in the water-only system (Harley and Carrington 2001) for 5 kbar and 900 °C. This modelled curve terminates at 10.20 wt% H_2O in the melt when H_2O saturation is achieved

Modelling of activity functions of CO_2 in cordierite at 5 kbar and 900 °C

Key aims of this study were to constrain the uptake of CO_2 in cordierite as a function of aCO_2 in the system and hence define the maximum CO_2 content attainable in cordierite at 5 kbar and 900 °C. The latter could not be done directly as our experiments only contained mixed H_2O–CO_2 fluids; experiments with pure CO_2 fluids would have not produced melt at this pressure and temperature. The approach to be used, therefore, is to calculate the maximum cordierite CO_2 content from the experimental data using independently-constrained calibrations of the a–X relations for H_2O in cordierite and melt. This can be accomplished via extrapolation of these a–X relations to the condition where $aH_2O = 0$ ($aCO_2 = 1$). From calculated values of aH_2O for experimental cordierite-melt pairs at fluid-saturation, aCO_2 can be determined by solving the equation of state for H_2O–CO_2 fluid mixing at the P–T of interest, consistent with the Gibbs–Duhem relation. With aCO_2 calculated from the phase water contents in this way, the variation of CO_2 in cordierite with aCO_2 can be assessed through the adoption of an appropriate volatile incorporation model for cordierite.

Calculation of aH_2O and aCO_2 from melt and cordierite H_2O data

Following Harley and Carrington (2001), the relationship between aH_2O and the solubility of H_2O in relevant granitic melts at a specified P–T condition is closely approximated by the 'Burnham-type' model (Burnham and Nekvasil 1986):

$$aH_2O = k_w(X_w)^2 \quad \text{for } X_w \le 0.5 \text{ and}$$
$$aH_2O = 0.25k_w[\exp((6.52 - (2667/T)).X_w)] \quad \text{for } X_w > 0.5 \qquad (6)$$

where X_w is the mole fraction of water in a melt calculated with 8-oxygens per formula unit and k_w is a P–T dependent coefficient. In this case k_w is extracted from

the H_2O-system cordierite-melt experiments of Harley and Carrington (2001), rather than calculated from the k_w model expressions of Burnham (1994), as the former were conducted under equivalent P–T conditions and in an analogous compositional system. At 5 kbar and 900 °C, the melt H_2O contents at fluid saturation, measured and modelled in Harley and Carrington (2001: 10.2 wt% H_2O), define k_w to be 2.42.

The maximum H_2O-contents of cordierite coexisting with pure H_2O have now been successfully determined at 3–7 kbar to 1,000 °C. Harley and Carrington (2001) modelled the cordierite saturation hydration data (Mirwald et al. 1979; Boberski and Schreyer 1990; Mukhopadhyay and Holdaway 1994; Carey 1995; Carrington and Harley 1996; Skippen and Gunter 1996; Harley and Carrington, 2001) together with their undersaturation data. This modelling demonstrates that the relation between aH_2O and the H_2O content of cordierite, governed by equilibrium (1), can be expressed as

$$aH_2O = z_w.[n/(1-n)] \quad (7)$$

where n is the number of molecules of H_2O per formula unit of cordierite, and z_w is a P–T dependent coefficient. At 5 kbar and 900 °C, the H_2O saturation value of n, defined by Harley and Carrington (2001), is 0.6 molecules per formula unit, such that z_w is 0.6667.

Using these values of k_w and z_w and the a-X relations for melt and cordierite respectively, we can produce pairs of calculated aH_2O values for each Crd–melt experiment conducted at 5 kbar and 900 °C. Furthermore, aCO_2 in the fluid-saturated two-component H_2O–CO_2 system is not independent of aH_2O, but rather a function of it. Hence, the aH_2O pairs can be converted to pairs of aCO_2 values pertaining to each experiment, through solution of the Gibbs–Duhem relation and taking non-ideal, P–T dependent fluid-mixing properties into account. In this study we have adopted the asymmetric regular solution approximation to the modified Redlich–Kwong equation of state for H_2O–CO_2 mixing as formulated by Holland and Powell (1990).

Maximum CO_2 content of cordierite

Defining m as the number of molecules of CO_2 per formula unit in cordierite, and using a one molecule per formula unit one-site model, consistent with the hydration model (7) referred to above

$$aCO_2 = z_c[m/(1-m)] \quad (8)$$

where z_c is a P–T sensitive coefficient that is the CO_2-system analogue of z_w. However, unlike the H_2O-system, z_c cannot be calculated directly from data available at unit aCO_2.

In our experiments $m/(1–m)$ is evaluated from the measured cordierite CO_2 data. Hence a plot of $m/(1–m)$ versus aCO_2, calculated as described above from the cordierite or melt H_2O contents, demonstrates a good linear fit consistent with the predicted relationship between cordierite CO_2 contents and the CO_2 activity (Fig. 3). The best-fit line through the data can be extrapolated to $aCO_2 = 1$ ($aH_2O = 0$) in order to evaluate m_{sat}, the saturation number of CO_2 molecules in cordierite in the H_2O-free subsystem. At 5 kbar, 900 °C and $aCO_2 = 1$, m_{sat} is found to be 0.16 ± 0.01 molecules of CO_2 per formula unit of cordierite.

Intermediate H_2O–CO_2 compositions

Once the maximum CO_2 content of cordierite at 5 kbar and 900 °C has been established as shown above a value for z_c can be determined at $aCO_2 = 1$ from

$$z_{c(P,T)} = (1 - m_{sat})/m_{sat} \quad (9)$$

Thus, $z_{c(P,T)}$ at 5 kbar and 900 °C is calculated as 5.25, whereas $z_{w(P,T)}$ evaluated previously for this P–T is 0.667. Using these data and the relations (7) and (8), the expressions:

$$aH_2O = 0.667.[n/(1-n)]$$
$$aCO_2 = 5.25.[m/(1-m)]$$

can be applied to calculate the channel volatile contents (n, m) of cordierite at intermediate fluid compositions (i.e. for compatible aH_2O–aCO_2 pairs consistent with the non-ideal fluid mixing model). The results of this calculation, shown by the lines in Fig. 4, agree well with the original raw data expressed in terms of m and n.

Comparison with previous experimental work

There are no other complete data sets from previous work at 5 kbar and 900 °C. Johannes and Schreyer

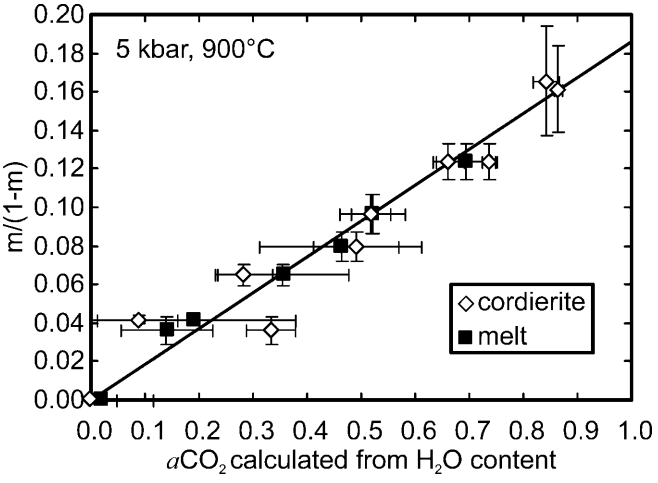

Fig. 3 A plot of the activity function of cordierite as $m/(1–m)$ versus the activity of CO_2 calculated from the aH_2O data. The *line* is the best fit line through the points and its value at $aCO_2 = 1$ allows us to estimate m_{sat} in the H_2O-absent case

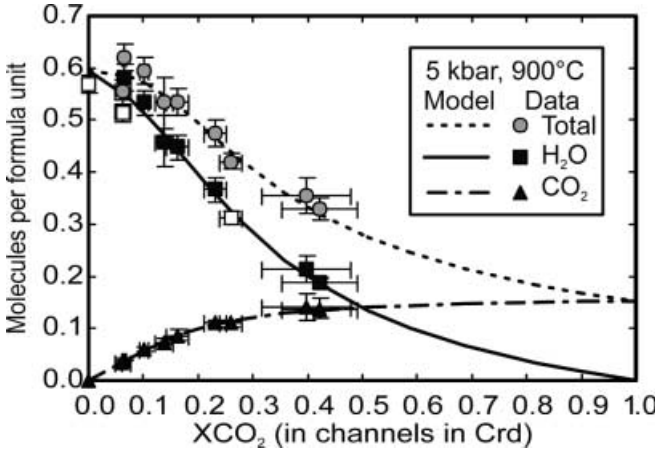

Fig. 4 Variation of the volatile composition in the cordierite channels with fluid-saturated, intermediate composition H_2O–CO_2 fluids. The *lines* show the modelled values agree well with the original raw data. *Closed symbols* H_2O measured in negatives; *open symbols* H_2O measured in positives; *triangles* CO_2; *circles* total number of molecules per formula unit

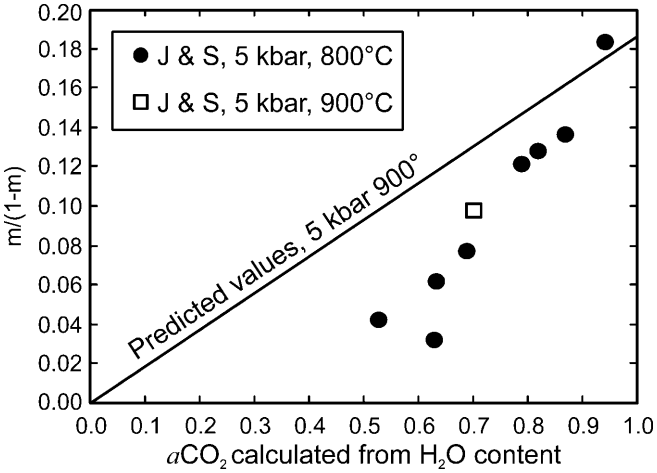

Fig. 5 A plot of $m/(1–m)$ against aCO_2 calculated from the aH_2O for the 5 kbar 800 and 900 °C data of Johannes and Schreyer (1981). The *line* shows our predicted values for 5 kbar and 900 °C. The equivalent line for 5 kbar and 800 °C should lie at slightly higher $m/(1–m)$ values

(1981) ran one experiment at 5 kbar and 900 °C, but otherwise the closest full set is their data at 5 kbar and 800 °C on their cordierite B starting material. We have taken these data and estimated the aCO_2 values from the aH_2O for their experiments using the methods we applied to our data (described above). The parameter z_w is again derived from the saturation data in the CO_2-free system (Harley and Carrington, 2001). The aCO_2 calculated from the cordierite H_2O content data in Johannes and Schreyer (1981) are plotted against their $m/(1–m)$ for both P–T conditions in Fig. 5. For comparison our best-fit line from Fig. 4 at 5 kbar and 900 °C is also shown on the plot. The equivalent line for 5 kbar and 800 °C should be at slightly higher $m/(1–m)$ values as there is a slight decrease in the CO_2-content of cordierite with increasing temperature (Johannes and Schreyer 1981 Fig. 5). At the higher CO_2 end of the graph Johannes and Schreyer's data points at 5 kbar and 800 °C agree more closely with our predictions. However, at intermediate CO_2 activities their data are significantly CO_2-poor compared with our predicted values. Their data including the 5 kbar 900 °C point do lie on a fairly linear trend, but one with a large negative intercept at $aCO_2 = 0$. The scattered 5 kbar, 800 °C data of Johannes and Schreyer is difficult to explain, but may suggest poor attainment of equilibrium, perhaps reflecting slow filling of cordierite channels with CO_2 compared with run duration, or variable re-equilibration on cooling and quenching. The results of our NKFMASH–CO_2 study do not account for chemical variations in any other components in the cordierite channels. This may partly explain the discrepancies found in relation to previous works. Nevertheless, plots such as Fig. 5 demonstrate that the H_2O and CO_2 data reported from the previous experiments are often internally inconsistent and should be treated with caution.

Comparison with previous models and applications for fluid saturation in cordierite

Kurepin (1984) produced a model for the P–T dependence of CO_2 uptake in cordierite based at least in part on the Johannes and Schreyer (1981) data set. This model implies a double-link between aCO_2 and $m+n$, as the formulation for CO_2–cordierite/volatile-free-cordierite is given as $m/(1–m–n)$. However, even with this interdependence between m and n, the Kurepin (1984) model does not fit the data for either cordierite A or B of Johannes and Schreyer (1981) particularly well.

A comparison of our model with that of Kurepin (1984) at 5 kbar and 900 °C is shown in terms of molecules of CO_2 (m) versus molecules of H_2O (n) per formula unit in Fig. 6. The predicted volatile contents differ significantly at both the high-CO_2 and high-H_2O ends, in part because of the different end member saturation values used. In the H_2O system, n from Harley and Carrington (2001) is greater than the fit to Mirwald et al. (1979) used by Kurepin (1984). In contrast, m extrapolated from our 5-kbar, 900 °C data in H_2O–CO_2 (this work) is less than that modelled by Kurepin (1984) from the Johannes and Schreyer (1981) cordierite A data. The overall curvature of the saturation surface is greater in our model, with the Kurepin (1984) model yielding an almost linear relation of m to n that does not fit our measured m–n relationship (Fig. 6) nor the data of Johannes and Schreyer (1981) in detail. When considered in detail it is apparent that the formulation used by Kurepin (1984) is incorrect as it implicitly involves a coupling between m and n, and hence aCO_2 and aH_2O. This coupling does not exist if a free fluid phase is absent (i.e. in fluid absent conditions) or indeed if the H_2O–CO_2 fluid phase is diluted by other components that may or may not enter cordierite (e.g. N, Ar, dissolved species). The formulation used by Kurepin (1984) over-defines

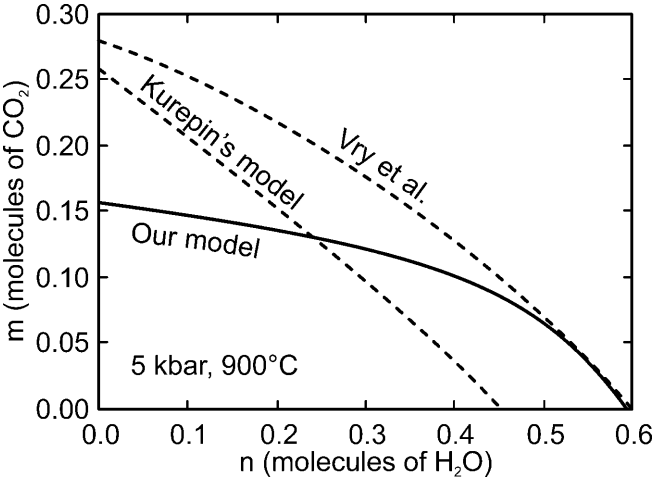

Fig. 6 A comparison of the co-variance of H_2O and CO_2 at fluid saturation for the models of Kurepin (1984), Vry et al. (1990) and the one proposed here

the system and hence is not appropriate for fluid activity calculations using cordierite H_2O–CO_2 contents.

The problems inherent in the Kurepin (1984) formulation are well illustrated by consideration of hypothetical fluid-undersaturated cordierites formed at 5 kbar and 900 °C with $n = 0.3$. Using our formulation $[n/(1–n)]$, aH_2O is 0.29 and independent of the amount of CO_2 in the cordierite, which could vary in the range $0 \leq m < 0.13$ before fluid saturation is reached (Fig. 6). In contrast, in the Kurepin (1984) model, aH_2O increases as CO_2 is added to the cordierite, from 0.29 at $m = 0$ to 0.323 at $m = 0.08$, the saturation m value obtained for $n = 0.3$ if the Kurepin (1984) $(1–m–n)$ denominator is used. This correlation between aH_2O and aCO_2 contravenes the phase rule as it implies that cordierites with two distinct values of n would define the same aH_2O at fixed P–T simply if their CO_2 contents were different. In short, the assumption of closure between anhydrous-cordierite, H_2O–cordierite and CO_2–cordierite inherent in the Kurepin (1984) model does not apply because cordierite can be volatile-undersaturated, as demonstrated conclusively by Carrington and Harley (1996). At saturation, the exchange reaction (3) ensures that as aCO_2 and m rise then aH_2O and n decrease for any specified P–T condition.

Vry et al. (1990) have also modelled the saturation H_2O–CO_2 contents of cordierite by combining selected experimental constraints including the H_2O-system data of Mirwald and Schreyer (1977) and Armbruster and Bloss (1980), the cordierite A H_2O–CO_2 results of Johannes and Schreyer (1981), and the CO_2-system cordierite results of Armbruster and Bloss (1982). The Vry et al. (1990) model uses the simplification that the percentage decreases in channel occupancy with XCO_2 (Crd) as modelled at 5 kbar and 600 °C are also applicable at all high-grade P–T conditions. This implicitly assumes that the isopleths of n (H_2O) and m (CO_2) in cordierite have both equal slopes and relative spacings in P–T space, which unfortunately is not the case. Figure 6 shows a comparison of our model with that of Vry et al. (1990) at 5 kbar and 900 °C in terms of molecules of CO_2 (m) versus molecules of H_2O (n) per formula unit. In this comparison we have used our value of $n = 0.6$ for the end point in the H_2O-system for Vry et al.'s model. Vry et al. compared models with different H_2O-system isopleths taken from a number of sources as illustrated on their Fig. 10. At 5 kbar, 900 °C these isopleths give approximate values of n of 0.42 (Helgeson et al. 1978), 0.55 (Mirwald et al. 1979) and 0.66 (Mirwald and Schreyer 1977; Armbruster and Bloss 1980). Vry et al.'s model and our model diverge progressively as XCO_2 (Crd) increases and n is reduced. The value of m extrapolated from our 5 kbar, 900 °C data in H_2O–CO_2 (0.16) is significantly less than that obtained using the approach of Vry et al. (1990: 0.28 molecules per formula unit.), which itself is even higher than that calculated using Kurepin (1984).

The net effect of the above comparisons is that, at 5 kbar and 900 °C, the saturation CO_2 content and H_2O–CO_2 contents of cordierite with high channel XCO_2 are lower than previously thought. This impacts upon the arguments put forward by Vry et al. (1990) to explain the apparently low total volatile contents, for specified P–T conditions of equilibration, of many of the cordierites reported in their study. Vry et al. (1990) considered that loss of volatiles during uplift and cooling was typical of most cordierites as their model suggested large volatile deficiencies for various cordierites from a range of environments. Such volatile leakage is no longer required to explain the volatile compositions of many of the CO_2-richer cordierites tabulated by Vry et al. (1990), although several examples of CO_2-poor cordierites are still volatile-deficient and hence imply some degree of volatile loss and/or equilibration under volatile-deficient conditions (Harley and Carrington, 2001). Whilst volatile leakage can explain the low channel volatile contents measured in some cordierites, it is clearly necessary to evaluate this for individual cases using the spatial resolution provided by SIMS to test for intra- and intergrain variability and zoning in H_2O and CO_2. Natural cordierite volatile content data can only be explicitly compared with the experimental cordierite data if the shifts of the modelled saturation curves, depicted in Figs. 4 and 6, with pressure and temperature, are taken into account (Harley et al. 2001).

A further key implication of the new experimental results is that our model predicts that fluid-saturated cordierites with channel $XCO_2 > 0.25$ imply aCO_2 of > 0.7 whereas the Kurepin (1984) and Vry et al. (1990) models yield lower aCO_2, in the range 0.4–0.45 for the same channel XCO_2 (Fig. 7). A good example of this effect is provided by cordierite that coexists with calcite in a 'reaction rock' from Finmark, Norway, which preserves channel XCO_2 of 0.75 and is inferred to have been formed in equilibrium with a near-pure CO_2 fluid (Armbruster et al. 1982). If the aCO_2–XCO_2 relations depicted on Fig. 7 are essentially independent of pres-

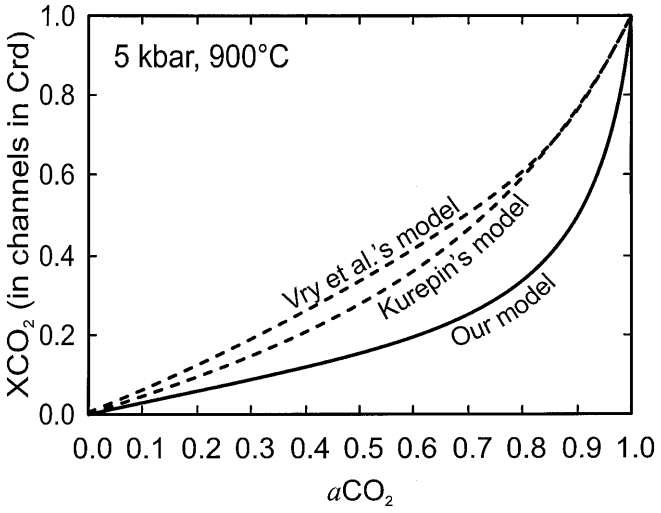

Fig. 7 The channel XCO_2 measured in a fluid-saturated cordierite would lead to a significant underestimate of the aCO_2 using either the model of Kurepin (1984) or Vry et al. (1990) in comparison to ours

sure and temperature, the aCO_2 for the Armbruster et al. rock is calculated as 0.96 using our calibration compared with 0.88 using the *a*–X relations of Kurepin and Vry et al.

Conclusions

The experimental data obtained here at 5 kbar and 900 °C demonstrate that the uptake of CO_2 by cordierite has a negligible effect on the distribution of H_2O between cordierite and coexisting melt (D_w) described by Harley and Carrington (2001). Incorporation of CO_2 into cordierite can be modelled simply by using a one-site formulation with aCO_2 being proportional to $m/(1-m)$, where m is the number of molecules of CO_2 per formula unit of cordierite, and does not follow the coupled H_2O–CO_2 model developed by Kurepin (1984) and subsequently applied by other workers. Most importantly, our self-consistent results show that the maximum CO_2 content of cordierite (i.e. at $aCO_2 = 1$) is significantly less than previously modelled for the experimental conditions. As a consequence, volatile-saturation in CO_2-bearing cordierites may be more common than previously inferred, and the aCO_2 of fluids associated with the equilibration of such cordierites may be greater than previously calculated for measured cordierite channel compositions.

The production of similar cordierite H_2O–CO_2 data for a variety of experimental conditions will ultimately allow the saturation CO_2 contents of cordierite to be modelled and evaluated over the range of P–T conditions of crustal metamorphism, and hence provide both aH_2O and aCO_2 estimates from cordierites such as those considered here. Such polybaric–polythermal experimental data will be described and modelled in a further paper that builds upon the analysis presented herein.

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References

Armbruster T, Bloss FD (1980) Channel CO_2 in cordierites. Nature 286:140–141

Armbruster T, Bloss FD (1982) Orientation and effects of channel H_2O and CO_2 in cordierite. Am Mineral 67:284–291

Armbruster T, Schreyer W, Hoefs J (1982) Very high CO_2 cordierite from Norwegian Lapland: mineralogy, petrology and carbon isotopes. Contrib Mineral Petrol 81:262–267

Barbey P, Macaudiere J, Nzenti J (1990) High-pressure dehydration melting of metapelites. J Petrol 31:401–427

Blank JG, Brooker RA (1994) Experimental studies of CO_2 in silicate melts: solubility, speciation and stable carbon isotope behaviour. Rev Mineral 30:157–186

Boberski C, Schreyer W (1990) Synthesis and water contents of Fe^{2+}-cordierites. Eur J Mineral 2:565–584

Burnham CW (1994) Development of the Burnham model for prediction of H_2O solubility in magmas. In: Carroll MR, Holloway JR (eds) Volatiles in magmas. Mineral Soc Am, Rev Mineral 30:123–129

Burnham CW, Nekvasil H (1986) Equilibrium properties of granitic pegmatite magmas. Am Mineral 71:239–263

Carey JW (1995) A thermodynamic formulation for hydrous cordierite. Contrib Mineral Petrol 119:155–165

Carrington DP, Harley SL (1995) Partial melting and phase relations in high-grade metapelites: an experimental petrogenetic grid in the KFMASH system. Contrib Mineral Petrol 120:270–291

Carrington DP, Harley SL (1996) Cordierite as a monitor of fluid and melt water contents in the lower crust: an experimental calibration. Geology 24:647–650

Clemens JD (1993) Experimental evidence against CO_2-promoted deep crustal melting. Nature 363:336–338

Fogel RA, Rutherford MJ (1990) The solubility of CO_2 in rhyolitic melts: a quantitative FTIR study. Am Mineral 75:1311–1326

Goldman DS, Rossman GR, Dollase WA (1977) Channel constituents in cordierite. Am Mineral 62:1144–1157

Harley S (1994) Cordierite as a sensor of fluid and melt distribution in crustal metamorphism. Mineral Mag 58A:374–375

Harley SL, Carrington DP (2001) The distribution of H_2O between cordierite and granitic melt: Improved calibration of H_2O incorporation in cordierite and its application to high-grade metamorphism and crustal anatexis. J Petrol (in press)

Harley SL, Thompson P, Buick IS, Hensen BJ (2001) Cordierite as a sensor of high grade metamorphic processes. J Metam Geol (in press)

Helgeson HC, Delany JM, Nesbitt HW, Bird DK (1978) Summary and critique of the thermodynamic properties of rock-forming minerals. Am J Sci 278A:1–229

Holland TJB, Powell R (1990) An enlarged and updated internally consistent thermodynamic dataset with uncertainties and correlations: the system K_2O–Na_2O–CaO–MgO–MnO–FeO–Fe_2O_3–Al_2O_3–TiO_2–SiO_2–C–H_2–O_2. J Metamorph Geol 8:89–124

Holloway JR, Blank JG (1994) Application of experimental results to C–O–H species in natural melts. Rev Mineral 30:187–230

Holtz F, Johannes W (1994) Maximum and minimum water contents of granitic melts. Lithos 32:149–159
Holtz F, Behrens H, Dingwell DB, Taylor RB (1992) Water solubility in aluminosilicate melts of haplogranite composition at 2 kbar. Chem Geol 96:289–302
Johannes W, Holtz F (1996) Petrogenesis and experimental petrology of granitic rocks. Springer, Berlin Heidelberg New York
Johannes W, Schreyer W (1981) Experimental introduction of CO_2 and H_2O into Mg-cordierite. Am J Sci 281:299–317
Kurepin VA (1984) H_2O and CO_2 contents of cordierite as an indicator of thermodynamical conditions of formation. Geokhimiya 8:1125–1134
Kurepin VA (1985) H_2O and CO_2 contents of cordierite as an indicator of thermodynamical conditions of formation. Geochem Int 22:148–156
Le Breton N, Schreyer W (1993) Experimental CO_2 incorporation in Mg-cordierite: non-linear behaviour of the system. Eur J Mineral 5:427–438
Mirwald PW, Schreyer W (1977) Die stabile und metastabile Abbaureaktion von Mg–cordierit in Talk, Disthen und Quartz und ihre Abhangigkeit vom Gleichgewichtswassergehalt des Cordierits. Fortschr Mineral 55:95–97
Mirwald PW, Maresch WV, Schreyer W (1979) Der Wassergehalt von Mg-cordierit zwischen 500 °C und 800 °C sowie 0.5 und 11 kbar. Fortschr Mineral 57:101–102
Mukhopadhyay B, Holdaway MJ (1994) Cordierite–garnet–sillimanite–quartz equilibrium: New experimental calibration in the system $FeO–Al_2O_3–SiO_2–H_2O$ and certain $P–T–XH_2O$ relations. Contrib Mineral Petrol 116:462–472
Newton R, Smith J, Windley B (1980) Carbonic metamorphism, granulites, and crustal growth. Nature 288:45–49
Papale P (1997) Thermodynamic modelling of the solubility of H_2O and CO_2 in silicate liquids. Contrib Mineral Petrol 126:237–251
Petersen JW, Newton RC (1990) Experimental biotite–quartz melting in the KMASH–CO_2 system and the role of CO_2 in the petrogenesis of granites and related rocks. Am Mineral 75:1029–1042
Santosh M, Harris NBW, Jackson DH, Mattey DP (1990) Dehydration and incipient charnockite formation: a phase equilibria and fluid inclusion study from south India. J Geol 98:915–926
Schmulovich KI, Graham CM (1996) Melting of albite and dehydration of brucite in H_2O–NaCl fluids to 9 kbar and 700–900 °C: implications for partial melting and water activities during high pressure metamorphism. Contrib Mineral Petrol 124:370–382
Schreyer W (1985) Experimental studies on cation substitutions and fluid incorporation in cordierite. Bull Mineral 108:273–291
Skippen GB, Gunter AE (1996) The thermodynamic properties if H_2O in magnesian and iron cordierite. Contrib Mineral Petrol 124:82–89
Stevens G, Clemens JD (1993) Fluid-absent melting and the roles of fluids in the lithosphere: a slanted summary? Chem Geol 108:1–17
Stevens G, Clemens JD, Droop GTR (1995) Hydrous cordierite in granulites and crustal magma production. Geology 23:925–928
Thompson P, Harley SL, Carrington DP (2001) Sodium and potassium in cordiente – a potential thermometer for melts? Eur J Mineral (in press)
Vielzeuf D, Holloway JR (1988) Experimental determination of the fluid-absent melting relations in the pelitic system. Consequences for crustal differentiation. Contrib Mineral Petrol 98:257–276
Vry JK, Brown P, Valley J (1990) Cordierite volatile content and the role of CO_2 in high-grade metamorphism. Am Mineral 75:71–88
Waters DJ, Whales D (1984) Dehydration melting and the granulite transition in metapelites from southern Namaqualand, S. Africa. Contrib Mineral Petrol 88:269–275
Watt GR, Harley SL (1993) Accessory phase controls on the geochemistry of crustal melts and restites produced by dehydration melting. Contrib Mineral Petrol 114:550–566