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# The influence of NaCl-H<sub>2</sub>O fluids on reactions between olivine and plagioclase: An experimental study at 0.8 GPa and 800–900 $^{\circ}$ C

# Thomas B. Grant<sup>a,b,\*</sup>, Daniel E. Harlov<sup>a,c</sup>

<sup>a</sup> Deutsches GeoForschungsZentrum, Telegrafenberg, D-14473 Potsdam, FR, Germany

<sup>b</sup> Department of Geoscience and Petroleum, Norwegian University of Science and Technology (NTNU), 7491 Trondheim, Norway

<sup>c</sup> Department of Geology, University of Johannesburg, P.O. Box 524, Auckland Park, 2006, South Africa

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# ABSTRACT

The lower to middle continental and oceanic crust is dominated by mafic gabbroic rocks, which are variably metamorphosed at amphibolite-granulite facies conditions forming reaction rims or veins containing secondary pyroxenes, amphibole and phlogopite. Metamorphic fluids in the mid-crust are typically NaCl-rich brines. In this study, olivine and plagioclase were reacted with varying amounts of fluid (0-2 wt% added) that had compositions ranging from pure  $H_2O$  to NaCl solutions (0–2 mol) in a series of experiments using the piston cylinder apparatus at 0.8 GPa and temperatures from 800 to 900 °C. Coronas of clinopyroxene, clinopyroxene + amphibole, and clinopyroxene + phlogopite were formed. The thicknesses of reaction rims, i.e. the relative amount of reaction rim products, increase with the relative amount of fluid present in the system, and are therefore linked to the level of fluid saturation along grain boundaries and interphase boundaries. Samples with no added H<sub>2</sub>O, show little to no signs of reaction, indicating the necessity for fluids in initiating a reaction between olivine and plagioclase. The concentration of NaCl in the fluid also increases the rates of rim growth. At 900 °C and 2 wt% added fluid, Cl-rich hydrous dacite-trachyte melt compositions formed and are similar to low degree partial melts of oceanic crust. The Cl contents of secondary amphiboles are positively correlated with the FeO and K<sub>2</sub>O contents of the amphibole. Consumption of fluid during the formation of hydrous rim phases may lead to high Cl within transient fluid filled pores along grain boundaries, which may lead to locally Cl-rich amphiboles.

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# 1. Introduction

The bulk of the middle and lower continental crust is chemically equivalent to mafic gabbroic rocks (Christensen and Mooney, 1995; Rudnick and Fountain, 1995). Metamorphism at amphibolite- and granulite-facies conditions in the presence of late magmatic fluids or the presence of metamorphic fluids leads to the formation of secondary veins and reaction rims, commonly consisting of pyroxene and amphibole that replace primary olivine and plagioclase (Table 1). There is considerable evidence that mid-crustal fluids are NaCl-rich brines (e.g. Harlov, 2012; Kullerud et al., 2001; Manning and Aranovich, 2014; Markl and Bucher, 1998; Newton et al., 1998; Newton and Manning, 2010; Yardley and Graham, 2002). The lower oceanic crust is also dominated by olivine bearing-gabbros (e.g. see Dick et al., 2000) that are variably metamorphosed to amphibolite conditions in the presence of Clrich hydrothermal fluids (Coogan et al., 2001; Dick et al., 2000; Gillis and Roberts, 1999; Girardeau and Mevel, 1982; Manning et al., 1996).

E-mail address: thomas.grant@ntnu.no (T.B. Grant).

In the oceanic crust, the location of the magmatic-hydrothermal divide is critical in understanding processes related to late magmatic fluids or to the ingress of fluids by fracture-induced, downward flux of seawater (e.g. Coogan et al., 2001; Manning et al., 1996). The chemical composition of amphiboles are sensitive to whether they formed from a melt or from a fluid (e.g. Coogan et al., 2001; Gillis, 1996; Gillis and Meyer, 2001). In both the oceanic crust and continental crust, gabbroic rocks are metamorphosed by Cl-rich aqueous fluids under sub-solidus amphibolite facies conditions forming secondary amphibole (Coogan et al., 2001; Dick et al., 2000; Gillis and Roberts, 1999; Girardeau and Mevel, 1982; Manning et al., 1996).

The influence of fluids for initiating metamorphic reactions is well documented (Carlson, 2010; Gardés et al., 2012; Milke et al., 2013; Rubie, 1986). Fluids act as a medium for reaction by lowering activation energies (Gardés et al., 2012; Rubie, 1986) and as powerful solvents, especially when salt-bearing, for aluminosilicate components that dissolve as polymerized clusters (Manning 2018), thereby increasing the mobility or diffusion rates of elements. Such behavior has been studied in detail in a range of other systems for example the forsterite-enstatite-quartz system (Gardés et al., 2012; Milke et al., 2013). This work reports on experimental reactions between olivine and plagioclase mixtures in





<sup>\*</sup> Corresponding author at: Deutsches GeoForschungsZentrum, Telegrafenberg, D-14473 Potsdam, FR, Germany.

Summary of selected literature data on reaction coronas formed between olivine and Plagioclase.

Study	Location	Ol	Pl	Rim assemblage	Pressure (GPa)	Temperature (°C)	Fluids	Magmatic / Metamorphic
Natural examples								
De Haas et al., 2002	Vestre Dale gabbro, Bamble sector, Norway	Fo64	An62-An48	Ol   Opx   Amp + - Opx + Spll (sympl)   Pl	0.71–0.77 (reg.)	750–840 (reg.)	Residual melt	Magmatic
Engvik et al., 2011	Bamble and Modum-Kongsberg sectors, Norway	Fo68-70	An44	Ol   Opx   Pl or Ol   Cpx + Mag (sympl)   pl	_	_	-	Magmatic
Gardner and Robins, 1974	Seiland Province, Northern Norway	-	-	Ol   Opx   Opx + Spl (sympl)   Pl	0.7-0.9	800-1000	-	Metamorhpic
Munz and Morvik, 1991	Modum complex, Norway	Fo71-49	An73-23	Ol   Opx   Amp + Spl   Grt   Pl	0.7-1.0	600-800	-	Metamorhpic
Gallien et al., 2012	Valle Fertil-La Huerta Ranges, San Juan Province, Argentina	Fo80-76	An99–95	Ol   Opx   Cpx + Spl (sympl)   Pl	0.5-0.65	<840	none	Metamorphic (solid state)
Gallien et al., 2012	Valle Fertil-La Huerta Ranges, San Juan Province, Argentina	Fo80-76	An99-95	Ol   Opx   Amp   Amp + Spl (sympl)   Pl	0.5-0.65	<770	Residual melt	Magmatic
Tomilenko and Kovyazin, 2008	Korosten' Pluton, Ukranian Shield	Fo37	An48.4	Ol   Opx   Opx + Cpx + Or (sympl)   Pl	>0.5	860-980	Relatively dry CO2 rich	Metamorhpic
Nishiyama, 1983	Mt. Ikoma, Japan	Fo63	An-rich	Ol   Amp + Spl   Pl	-	-	$H_2O$	Metamorphic (diffusion)
Johnson and Carlson, 1990	Adirondack Mountains, New York, USA	Fo50	An55	Ol   Opx   Cpx   Pl + Grt   Pl + Spl	0.65–0.8 (reg.)	650–800 (reg.)	CO <sub>2</sub>	Metamorphic (diffusion)
Markl et al., 1998 Ikeda et al., 2007	Lofoten, Norway Sefuri Mountains, NW Kyushu, Japan	Fa-rich	Albite	Ol   Opx   Grt + Opx   Pl + Kfs Ol   Opx   Pl	0.4–1.0 –	780–840 800–900	H <sub>2</sub> O (low %) -	Magmatic Metamorphic
Ikeda et al., 2007	Sefuri Mountains, NW Kyushu, Japan			Ol   Amp + Opx   Spl + Amp	-	600-710	H <sub>2</sub> O	Metamorphic
Cruciani et al., 2008	Sierra de San Luis, Argentina	Fo81-80		Ol   Cpx + Spl (sympl)   Pl	0.7-0.8	900		Metamorphic
Cruciani et al., 2008	Sierra de San Luis, Argentina	Fo81-80		Ol   Cpx + Spl (Sympl) to Amp + Spl (sympl)   Pl	0.7–0.8	740–790	H <sub>2</sub> 0	Metamorphic
Experiments								
Keller et al., 2008		Fo81	An84	Ol   Di + En   Al-Px + En   Grt   Zo + Crn   An	1.8	900	MnCl <sub>2</sub> (5 M) 1.1 wt%	melt present
Keller et al., 2008		Fo81	An83.6Ab16.2	Ol   Di + En   Al-Px + En   Grt   Zo + Crn + Ky   An	1.8	900	"dry"	melt present
Liu et al., 1997		Fo92	An100	Fo   En + Di + Spl   An	0.7	1000	<0.5 wt% H2O	subsolidus
Larikova and Zaraisky, 2009		Fo89	An51	Ol   En + Ged   Hbl + Phlog   Pl	0.5	700	0.1 M NaCl - H2O	subsolidus
Ronde and Stünitz, 2007		Fo93	An92	Ol   Spl + Cpx   Opx + - Grt   Pl	1.0-1.6	900	"dry" (30 ppm H2O)	subsolidus

Pressure is in GPa, Olivine compositions are in their forsterite content, and Plagioclase their anorthite content. Temperature is in °C. Mineral abbreviations are in accordance with Whitney and Evans (2010). Sympl = symplectite, Al-Px = an Al-rich pyroxene, – refers to an absence of information for this field and 'reg.' = regional metamorphic conditions.

the presence of different fluid:rock ratios and different fluid compositions ( $H_2O$  and NaCl- $H_2O$  solutions) at 0.8 GPa and 800–900 °C. The pressure and temperature conditions of these experiments are within the ranges calculated for natural corona reactions (see Table 1) and are appropriate for the lower continental crust. The aim of this study is to replicate the corona assemblages summarized in Table 1 but also, in a more general sense, to explore how olivine and plagioclase react in the presence of NaCl- $H_2O$  solutions at lower crustal pressures. The pressures are notably higher than those in the lower oceanic crust... Our experiments can be compared to those of Currin et al. (2018), which are at pressure conditions that correspond to the lower oceanic crust.

### 1.1. Formation of amphibole-bearing coronas in continental gabbros

A common feature observed in mafic cumulate rocks is the formation of reaction rims / coronas between primary olivine and plagioclase (Cruciani et al., 2008; De Haas et al., 2002; Engvik et al., 2011; Gallien et al., 2012; Gardner and Robins, 1974; Ikeda et al., 2007; Johnson and Carlson, 1990; Markl et al., 1998; Munz and Morvik, 1991; Nishiyama, 1983; Tomilenko and Kovyazin, 2008). The most common rim sequence in the coronas is an inner shell of orthopyroxene at the olivine interface and an outer symplectitic shell composed of either clinopyroxene + spinel or amphibole + spinel at the plagioclase interface. Some natural examples of coronas between olivine and plagioclase are summarized in Table 1. The mineralogy of the coronas, however, varies significantly from one locality to the next, and the reasons for this are unclear. Differences in the composition of the system, fluid:rock and/or fluid:melt ratios, and pressure-temperature conditions (that may cover the magmatic-hydrothermal divide) all affect the physical and chemical properties of the rim phases. These differences may thus determine the involved diffusion and/or reaction mechanisms as well as the kinetics of fluid:rock and/or fluid:melt interaction processes. Some authors report that coronas form by magmatic processes, which may involve residual interstitial melts that react with both the olivine and plagioclase (De Haas et al., 2002; Gallien et al., 2012), infiltration of late magmatic fluids (Markl et al., 1998), or heating during the intrusion of hotter and younger batches of melt (Griffin et al. 2013) into an already crystallized gabbro. Alternatively, many authors suggest that the coronas may form by metamorphic processes (Ikeda et al., 2007; Munz and Morvik, 1991) involving crustal fluids (Tomilenko and Kovyazin, 2008) or solid state diffusion (Joesten, 1986; Johnson and Carlson, 1990; Nishiyama, 1983). Finally, the reactions may form simply by changing P-T-X conditions where the assemblage olivine + plagioclase becomes unstable due to decreasing temperature and/or increasing pressure (Gardner and Robins, 1974; Green and Ringwood, 1972; Irving and

Green, 1970; Kushiro and Yoder Jr, 1966). Multistage models have also been proposed (Gallien et al., 2012). Although the coronas are very common, they are not ubiquitous. Even within a single intrusion, coronas can be present in some localities but not in others (Grant et al., 2016b; Tomilenko and Kovyazin, 2008). Tomilenko and Kovyazin (2008) therefore suggested that the coronas formed by reactions with fluids and that local variations in whether the coronas developed or not were related to the presence or absence of fluids. Furthermore, there is limited experimental data within the olivine - plagioclase system, such as variations in the mineralogy of coronas with different pressures, temperatures or fluid compositions (Keller et al., 2008; Larikova and Zaraisky, 2009; Liu et al., 1997; Ronde and Stünitz, 2007). In summary, there is a significant database regarding the petrography and mineral chemistry of natural samples from a variety of locations where coronas between olivine andplagioclase are observed. Different authors propose very different models for the formation of very similar corona assemblages. If coronas between olivine and plagioclase are to be useful as petrogrentic indicators of metamorphic or magmatic events, the conditions under which they form in terms of pressure, temperature and fluid conditions need to be better constrained.

#### 2. Material and methods

### 2.1. Experimental method

Twelve experiments in the olivine-plagioclase-fluid system were conducted at pressures of 0.8 GPa and between 800 and 900 °C. In each experiment, the sample charge consisted of isolated San Carlos olivine crystal fragments in a plagioclase matrix (+ minor chloroapatite) with an added fluid component. Fluids ranged from 0 to 2 wt% (of sample charge) of double distilled water or 2 wt% of 2 M NaCl solution (0.035  $X_{NaCl}$ ). Compositions of starting materials are given in Table 2 and the details of the run conditions are given in Table 3.

The starting materials included single crystals of San Carlos olivine, single crystal hortonolite olivine, and a partially crushed sample of gabbro from the Bamble Sector, SE Norway. The preparation of these materials for the experiments is as follows. A single crystal of inclusion-free San Carlos olivine was crushed using a metal pestle and mortar. Crystal fragments with sizes between 250 and 500 µm were separated from the crushed material using sieves. A second, more Fe-rich hortonolite

#### Table 2

EMP compositions of starting materials (wt%).

	Plagioclase	San Carlos olivine	Bushveld olivine	Apatite
N	8	40	6	1
SiO <sub>2</sub>	52.89 (1.55)	39.43 (0.30)	34.16 (0.42)	-
$Al_2O_3$	30.44 (0.92)	-	0.02 (0.02)	-
FeO	0.11 (0.15)	8.47 (0.19)	47.33 (2.26)	0.04
MnO	0.02 (0.04)	-	0.59 (0.15)	0.05
NiO	-	0.38 (0.02)	-	-
MgO	0.02 (0.05)	52.07 (0.30)	19.21 (2.04)	-
CaO	12.45 (0.97)	0.11 (0.01)	0.05 (0.03)	54.43
Na <sub>2</sub> O	4.46 (0.60)	-	-	-
K <sub>2</sub> O	0.05 (0.02)	-	-	0.03
$P_2O_5$	0.02 (0.01)	-	-	42.46
F	-	-	-	-
Cl	-	-	-	1.09
Total	100.99	100.46	101.42	98.12
	0.64			
An	0.61	-	-	-
Ab	0.39	-	-	-
Kfs	-	-	-	-
Fo	-	0.91	0.42 (0.04)	-

Values in brackets are the standard deviation of the averages, N = number of analyses used for the average and – refers to values that were below the detection limits. Olivine analyses are from Grant et al. (2014), who used the same single crystal of San Carlos olivine. olivine (Bushveld Complex, South Africa) was also used in one experiment (OP012) to test the effect of varying Fe-content on rim formation. A piece of the sample was crushed and olivine grains were picked out using tweezers. To prepare the matrix, anorthositic plagioclase (Table 2) grains were hand-picked from a sample of partially crushed gabbro from Kragerø, Bamble Sector, SE Norway. The plagioclase grains were ground to a fine powder (<50  $\mu$ m) in ethanol using an agate pestle and mortar. This powder consisted of >96% anorthitic plagioclase, 2–3% chlorapatite, and 1–2% Cl-rich calcic amphibole.

Starting materials were loaded into Pt capsules (length 10 mm, outer diameter 3 mm, wall thickness 0.2 mm). A PUK 3 (Lampert) arc welder was used to seal all capsules at one end before loading the sample materials. Fluids (double distilled water or 2 M NaCl solution) were added to the capsule first via a micro-syringe. The capsules were then half filled with the plagioclase powder, before several single olivine crystal fragments were added. Plagioclase powder was added to completely fill the capsule and then the capsule was arc welded shut. All capsules were weighed after the final weld, placed in a 100 °C oven for over an hour, and then weighed again to verify any potential fluid-loss. Only those capsules for which no weight loss was observed were used. In the case of experiments OP001 and OP005, where no fluid was added, the plagioclase powder was dried for 24 h before at 100 °C before being loaded into the capsule, whereas OP009 was dried at 200 °C (Table 3).

Experiments conducted the were at Deutsche GeoForschungsZentrum Potsdam in a Johannes type piston cylinder apparatus (Johannes, 1973; Johannes et al., 1971) using a CaF<sub>2</sub> pressure media, graphite cylindrical ovens, and Ni/Ni-Cr thermocouples (Table 3; Fig. 1). Pressures of 0.8 GPa, temperatures of 800 °C or 900 °C, and run duration of 8 days were used for all experiments. The CaF<sub>2</sub> parts were machine drilled to accommodate four vertical capsules within a single run. Each capsule was separated by a sheet of biotite so that the capsules do not become welded or attached to each other during the experiment and can easily be extracted after the experiment. The thermocouple junction was located approximately half way up along side the first of the Pt capsules (Fig. 1). Thermal gradients along the vertical capsules are estimated to be 40-50 °C at both 800 and 900 °C. Pressure was initially loaded to ~0.65 GPa before heating to 800 °C allowing the CaF<sub>2</sub> setup to expand to near 0.8 GPa followed by a final manual adjustment to 0.8 GPa. Temperature fluctuations were within 1–3 °C. At the end of each experiment, the temperature was turned off and the samples were cooled through the internal cooling system of the piston cylinder press. Thermocouples recorded quench rates in excess of 40 °C/s over a temperature range of 900–100 °C. Following cooling to room temperature, the pressure was unloaded gradually to avoid damage to the piston cylinder parts. After each experiment, the capsules were extracted, cleaned using a metal pick to remove any CaF<sub>2</sub> or biotite from the outside of the capsule and taking care not to lose any Pt from the capsule itself, and then weighed again. None of the capsules showed any reduction in weight, indicating no observable loss of volatiles at peak P-T conditions.

#### 2.2. Electron microprobe (EMP) analyses

Electron microprobe (EMP) analyses of the samples were made using a JEOL Hyperprobe JXA-8500F with a field-emission cathode at the GeoForschungsZentrum Potsdam. For olivine, orthopyroxene, amphibole, and clinopyroxene analyses, a 15 kV accelerating voltage and a 20 nA beam current was used. For plagioclase and chlorapatite, operating conditions were 10 kV accelerating voltage and 10 nA. Silicate, oxide, and metal standards (both synthetic and natural) were used. A 5 µm beam diameter was used for plagioclase, amphibole, and chlorapatite analyses whereas beam sizes of <1 µm were used for olivine, orthopyroxene, and clinopyroxene. Matrix corrections and data reduction were performed using software provided by JEOL. Alkalis were always analysed first, along with Al and Si, to avoid migration problems.

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Run conditions for experiments. Vein assemblage refers to secondary veins formed within the olivine single crystals (Grant et al., 2016a).

Name	Olivine	Temperature (°C)	Pressure (GPa)	% added fluid	Fluid composition	Duration (hrs)	Rim products	Rim thicknesss (µm)	No. Of rim measurements	Vein assemblage
OP001	San Carlos	800	0.8	0	-	192	Cpx   Cpx + Amp (sym)	12.2 (2.9)	25	-
OP002	San Carlos	800	0.8	0.51	H <sub>2</sub> O	192	Cpx + phlog	5.6 (1.0)	13	Cpx + Ol
OP003	San Carlos	800	0.8	2.04	H <sub>2</sub> 0	192	Amp	22.3 (2.3)	14	Орх
OP004	San	800	0.8	1.99	2 mol NaCl	192	Amp + phlog	-		Opx + Ol
OP005	San Carlos	900	0.8	0	-	192	Amp	10.8 (1.6)	14	-
OP006	San	900	0.8	0.55	H <sub>2</sub> O	192	Cpx + phlog	14.7 (1.9)	22	-
OP007	San	900	0.8	2.04	H <sub>2</sub> O	192	Amp	18.1 (2.7)	27	-
OP008	San	900	0.8	2.06	2 mol NaCl	192	Amp	35.6 (3.1)	25	-
OP009	San	800	0.8	0	-	192	no reaction	<<1		-
OP010	San	800	0.8	1.13	H <sub>2</sub> O	192	Amp + Cpx	7.9 (1.4)	14	Opx + Cpx
OP011	San	800	0.8	3.66	H <sub>2</sub> O	192	n/a	-		+ 01 -
OP012	Carlos Bushveld	800	0.8	1.86	H <sub>2</sub> 0	192	Срх	5.9 (1.2)	25	-

Counting times for all elements were 10 s on peak and background except for Na and K which had 5 s on peak and background. Detection limits were between 200 and 300 ppm. Tugtupite was used as the standard for Cl and F.

Three line scans were conducted using the JEOL JXA-8200 probe at the Freie Universität Berlin. Accelerating voltages of 15 kV, beam currents of 20 nA, focused beams of 1  $\mu$ m, and natural standards were used for all line scans.



Fig. 1. Sketch of the assembly used in the piston-cylinder experiments.

#### 2.3. Rim thickness measurements

Rim thicknesses were determined using the direct method, which involves measuring the rim thickness at different ( $\geq$ 13) points along the rim. Observable rim thicknesses can be greater than the actual rim thickness due to the orientation of rim interfaces with respect to the cut of the polished section. Measurements were therefore taken at places that had the thinnest rims. If all samples are measured in the same way utilizing this method, the data are comparable. For further discussion regarding this technique, see Liu et al. (1997) and Grant et al. (2014).

# 3. Results

# 3.1. Reaction rim assemblages

Reaction rim assemblages are summarized in Table 3. Images of reaction rims and other textural features in the experiments are shown in Fig. 2. In all experiments some porosity is visible in the plagioclase matrix, particularly along grain boundaries. Where reaction rims are present, the olivine-rim and plagioclase-rim interfaces are irregular and lobate, indicating partial dissolution of both olivine and plagioclase. All samples were analysed thoroughly initially using EMP for their rim mineralogy and matrix mineralogy.

#### 3.1.1. '800 °C – no added fluid

Two dried samples were run at 800 °C and 0.8 GPa. OP009, dried for 24 h at 200 °C, and shows no observable reaction with the plagioclase matrix (Fig. 2A). The interface between the olivine and plagioclase is relatively linear (compared to where reaction rims formed) although some pores and angular embayments are visible.

OP001 was dried for 24 h at 100 °C and has the following reaction rim sequence; clinopyroxene (<  $2 \mu m$ ) at the olivine interface, a middle rim of amphibole (3–4  $\mu m$ ) and an outer rim of amphibole + clinopyroxene symplectite (3–4  $\mu m$ ) at the plagioclase interface (Table 3; Fig. 2B). The symplectite consists of rods of clinopyroxene in a matrix of amphibole. Most of the clinopyroxene rods are highly irregular in shape and show a very weak orientation, whereas some rods are orientated nearly perpendicular to the olivine-rim interface. The wavelength



**Fig. 2.** High contrast back scatter electron (BSE) images of the reacted sample charges. Mineral abbreviations are according to Whitney and Evans, 2010. A – Sample OP009 (800 °C, no added fluid and dried at 200 °C). No apparent reaction rims are observed between the olivine interface and the plagioclase matrix. Pores are visible along plagioclase grain boundaries. B - Sample OP001 (800 °C, no added fluid and dried at 100 °C). Here, a reaction rim sequence of clinopyroxene at the olivine interface, a middle rim of amphibole and an outer rim of amphibole (matrix) + clinopyroxene (rods) symplectite at the plagioclase interface has formed. Pores are present in the plagioclase matrix. C – Sample OP006 (900 °C, with 0.55 wt% added double distilled water) close up image of the reaction rim which contains clinopyroxene and phlogopite. Some of the phlogopite grains have been plucked out during polishing. D – Sample OP005 (900 °C, no added fluid and dried at 100 °C). A reaction rim of just amphibole has formed between the olivine and plagioclase. Fores are observed in the plagioclase matrix and in a pore trail within the olivine single crystal. E - Sample OP006 (900 °C, with 0.55 wt% added double distilled water). A Reaction rim of clinopyroxene and phlogopite has formed between olivine and plagioclase. F – Sample OP007 (900 °C, with 0.24 wt% added double distilled water). A reaction rim of clinopyroxene and phlogopite has formed between olivine and plagioclase. Givine in the face of the mage) and the San Carlos olivine with Fo<sub>90</sub> (darker olivine at the top of the image) can be observed. The Bushveld olivine reacted to form a rim of clinopyroxene. Note the irregular and embayed olivine-clinopyroxene rim interface that is characteristic of all of the rims formed. H - Sample OP008 (900 °C, with 2.06 wt% added 2 mol NaCl solution). In this sample, melt formed within the plagioclase matrix, now present as glass. The glass contains numerous small vesicles with larger vesicles at the plagioclase-melt interface. The plagiocla

and periodicity of the rods are irregular. Some small (<<1  $\mu$ m) pores are observed within the reaction rim and at the olivine interface. Sample OP005 was also dried at 100 °C for 24 h but was run at 900 °C. In this sample, reaction rims (10–11  $\mu$ m) of mainly amphibole formed (Fig. 2C).

#### 3.1.2. 800 °C - with fluid added

At 0.5 wt%  $H_2O$  added, (OP002) rims of minor clinopyroxene and phlogopite formed with a thicknesses of around 8  $\mu$ m. Clinopyroxene appears to be concentrated at the olivine interface with phlogopite concentrated at the contact with the plagioclase (Table 3). The rim-olivine interface is very irregular and convoluted, as is the interface with plagioclase. In some areas, the rim branches into the plagioclase matrix along a grain boundary for around 10–20  $\mu$ m. Pores are also common along the plagioclase grain boundaries. A clinopyroxene vein into the olivine is also observed. This is about 20  $\mu$ m wide and locally associated with discrete zones of Fe-depleted olivine. Small pores are concentrated along the clinopyroxene-olivine interface.

With a  $H_2O$  content of 1.1 wt% (OP010), amphibole rims (with minor clinopyroxene) form with thicknesses of around 10  $\mu$ m (Table

3). Veins of orthopyroxene and minor clinopyroxene form within the interiors of the olivine. Contacts between pyroxenes and olivine are sharp but are lined with porosity and locally associated with fluid inclusion trails. The olivine adjacent to the fluid inclusions trails is often marked by irregular but diffuse Fe-depleted zones.

Increasing the water content to 2 wt%  $H_2O$  (OP003) led to the formation of thick (22.3 µm) reaction rims consisting of fine-grained amphibole only. For the more Fe-rich Bushveld olivine (OP012), under the same fluid conditions and temperatures as OP003, thinner 5.9 µm rims of amphibole form. From Fig. 2E, the amphibole rims around the Bushveld olivine appear to be thicker than those forming around an adjacent San Carlos olivine in the same sample (approximately 20 µm vs. 10 µm, respectively) (Table 3). Veins of amphibole into the olivine from the rims are observed as well as fluid inclusion trails in the olivine.

For the same bulk fluid content (2 wt%), but with 2 M NaCl solution (OP004), similar reacted rims developed again but the rims consist of amphibole and phlogopite. The phlogopite is fine grained but has been plucked and damaged by polishing, indicating that the rim material was particularly soft and highly porous. In all the experiments with

the highest amount of fluid added (2 wt%), the plagioclase matrix shows a high porosity.

#### 3.1.3. 900 °C - no added fluid

Despite being dried at 100 °C, reaction rims of amphibole + clinopyroxene around olivine (11 µm thick) formed in sample OP005 (Table 3; Fig. 2C). Clinopyroxene is slightly more abundant relative to amphibole. Porosity is present in the reaction rims and some fluid inclusion trails formed in the olivine. Pores are observed along plagioclase grain boundaries in the sample matrix (Fig. 2C), but the amount of pores appears to be less than in samples with higher added fluid contents (e.g. OP006, OP007, and OP008).

# 3.1.4. 900 °C - with fluid added

The addition of 0.5 wt% H<sub>2</sub>O (OP006) forms rims of amphibole + clinopyroxene that are similar to the rims formed in OP005 (no added fluid), though here the rims are thicker by several microns (Table 3; Fig. 2D). The plagioclase matrix is also noticeably more porous than OP005.

Experiment OP007 contained 2 wt% H<sub>2</sub>O. Continuous rims of amphibole formed around olivine with a thickness of around 18 µm. Olivine at the interface with the reaction rims is depleted in Fe over distances of <4 µm. Porosity is also present at the olivine-rim interface. Small pockets of glass are observed as an interstitial amorphous mass between plagioclase grains within the matrix of this sample. The glass pockets contain abundant, large rounded vesicles that are predominantly distributed along plagioclase-glass interfaces (similar to those in OP008; Fig. 2E). Plagioclase in contact with the glass is zoned.

The addition of a 2 M NaCl solution (OP008) at the same bulk fluid contents (2 wt%) formed similar reaction rims of amphibole around olivine but with greater thicknesses of 20 to 30 µm. Some porosity is observed in the reaction rims. Local depletion of Fe at the olivine interface also formed in this experiment. Glass pockets containing large vesicles were also observed in this sample (Fig. 2F).

# 3.2. Reaction rim thicknesses

Rims of different mineralogy cannot be directly compared. Amphibole dominated rims are separated from clinopyroxene dominated rims and the rim thicknesses are plotted against added fluid in wt% (Fig. 3). For amphibole-dominated rims, rim thicknesses appear to increase with an increase in the amount of fluid for experiments at 800 °C and 900 °C (Table 3). This is a feature of many other systems such as guartz-enstatite-forsterite (Gardés et al., 2012) or phonolite meltphlogopite-olivine (Grant et al., 2014). The presence of NaCl also appears to increase the rim thickness at 2 wt% fluid and at 800 °C. In samples where no fluid was added (OP001 and OP005) the rim thicknesses are greater at higher temperature (thicker rims in OP005 at 900 °C), but at 2 wt% added fluid the rim thicknesses at 800 and 900 °C are similar (Table 3). For clinopyroxene-dominated rims, there is no clear increase in rim thickness with added fluid content. Rim thicknesses at 0.5 wt% added fluid appear to be larger at 900 °C than at 800 °C.

### 3.3. Mineral and glass chemistry

#### 3.3.1. Plagioclase

The composition of the plagioclase matrix after the experiment is the same as that of the starting material (Table 2), indicating little to no modification of the plagioclase matrix during the experiments. This is the same for all samples.

#### 3.3.2. Amphibole

Representative EMP compositions are given in Supplementary Table 1. Amphibole compositions are pargasitic, except for those in sample OP003, which are magnesiohornblende in composition. Amphibole in OP003 are much poorer in Na + K in the A site. All amphiboles have lower Al/Si ratios or around 0.3 to 0.6 compared to the matrix plagioclase, which is between 0.6 and 0.8 (Fig. 4). OP008 shows extremely low Al/Si ratios of <0.5. All amphiboles show similar Na/(Na + Ca) ratios compared to matrix plagioclase (0.25–0.45), whereas sample OP003 is much lower (0.15–0.25). Amphiboles show some strong chemical trends with varying Cl contents. For example, a strong positive correlation is seen for Na + K in the A site (Fig. 4D), but a negative correlation is seen between Cl and  $X_{Mg}$  (= Mg/(Fe + Mg). The correlations are similar to those observed in natural amphiboles from continental and oceanic samples (Mathematican Ridge; Vanko, 1986, Mid Atlantic Ridge; Coogan et al., 2001, Hess Deep and Hole 735B; Gillis and Meyer, 2001) and continental samples (gabbronorite shear zone; Kullerud and Erambert. 1999; gneiss; Leger et al., 1996; eclogite; Liu et al., 2009, Tonalite-granitic; McCormick and McDonald, 1999).

# 3.3.3. Clinopyroxene

Clinopyroxene in the rims is diopsidic (Supplementary Table 2; Fig. 5) with high  $X_{Mg}$  values of 0.95, except for those in sample OP012, which contained Fe-rich olivine. These have much lower  $X_{\rm Mg}$  values of 0.61 to 0.88. Clinopyroxene in samples with <0.5 wt% added fluid (OP001 and OP002) appear to be higher in Si and Mg but lower in Al and Na compared to samples with >0.5 wt% added fluid (OP010 and OP012) that have higher Al and Na but lower Si and Mg (Fig. 5).

#### 3.3.4. Phlogopite

Phlogopite compositions are shown in Supplementary Table 3 and in Fig. 6. Phlogopite compositions vary from high Si + Mg and low Al, to





Fig. 3. Plot of measured rim thicknesses of amphibole and clinopyroxene dominated rim assemblages against the amount of added fluid.

# 84 **Table 4**

EMP glass compositions (wt%) from this study and partial melts of gabbros from experiments at 900 °C by Koepke et al. (2004).

	This stu (0.8 GPa	dy a, 900 ° <b>C</b> )	)	Koepke et al., 2004 (0.2 GPa, 900 °C)			
Sample	OP007	<b>OP007</b>	OP007	<b>OP008</b>	61a	101	923a
SiO <sub>2</sub>	63.74	63.32	63.18	63.26	67.38	62.33	66.40
$Al_2O_3$	23.00	23.08	22.84	23.99	17.02	22.43	18.03
FeO	-	0.09	0.11	0.19	4.09	3.09	4.27
MnO	-	-	0.08	0.16	0.09	0.03	0.12
MgO	1.76	1.82	1.67	2.69	1.87	2.19	2.30
CaO	3.69	3.77	3.90	3.22	5.61	5.14	5.28
Na <sub>2</sub> O	5.58	5.77	5.92	3.48	3.42	3.00	2.73
K <sub>2</sub> O	1.55	1.55	1.65	2.04	0.22	1.26	0.60
$P_2O_5$	0.37	0.33	0.33	0.49	0.16	0.40	0.17
F	-	-	-	-	-	-	-
Cl	0.28	0.27	0.33	0.47	-	-	-
Volatile	9.82	9.88	8.9	9.01			
Total	100	100	100	100	99.86	99.47	99.90
Melt fraction (%)	<2	<2	<2	<2	<10	<10	<10

compositions with high Al and low Si + Mg (Fig. 6 a, b). The phlogopite compositions do not vary consistently with the experimental conditions and a full range of compositions can even be observed in one sample (OP002). There is no consistent variation in Na or Cl with any other major element (Fig. 6 c, d). All phlogopite formed is highly magnesian (> 0.92 X<sub>Mg</sub>). The F contents of the phlogopite are below EMP detection limits but they do contain small amounts of Cl (up to 0.11 wt%). The highest Cl contents were observed in samples OP002 and OP006 (0.5 wt% added H<sub>2</sub>O) but were much lower in sample OP004, which contained 2 wt% added NaCl fluid. This could be due to the fact that the rims in OP002 and OP006 contain only clinopyroxene and phlogopite. Here, the Cl would only be partitioned into the phlogopite and not the clinopyroxene with which it is incompatible. In comparison,

sample OP004 contained both phlogopite and amphibole, which both would take Cl and thereby reduce the amount of Cl available to the phlogopite. In addition, Cl is more compatible with phlogopite that is richer in Fe (Leger et al., 1996). This would also be a factor in increasing the Cl content of the rim phlogopite as they are more Fe-rich in samples OP002 and OP006 compared to phlogopite in sample OP004. Chlorine appears therefore to be preferentially incorporated in the following order starting with the highest concentration: amphibole > phlogopite. Finally, it is also possible that Cl enrichment in phlogopite could be related to lower overall fluid saturation in experiments with 0.5 wt% added water (OP002 and OP006). This would be consistent with models of fluid consumption by reactions that lead to lower H<sub>2</sub>O saturation but higher Cl concentrations in the fluid (e.g. Kullerud, 1996; Kullerud et al., 2001; Markl et al., 1998).

#### 3.3.5. Apatite

Apatites from the Bamble sector, where the starting material is from, are known to be particularly Cl enriched (Nijland et al., 1993; also see starting material in Table 2). EMP analyses of matrix apatites (Supplementary Table 4) show that they retain their high Cl contents, except for apatite in sample OP001, which is anomalously high in F.

# 3.3.6. Glass

Glasses are only observed in samples at 900 °C that contained 2 wt% amounts of fluid (OP007 and OP008). EMP glass analyses are given in Table 4. The glasses are dacite-trachydacite in composition (on a volatile-free basis normalized to 100). They are significantly enriched in SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, and alkalis, but are depleted in MgO and FeO. For OP008, in the presence of an NaCl-bearing fluid, the glass is poorer in Na<sub>2</sub>O and richer in K<sub>2</sub>O than in OP007. The glasses in both samples contain around 0.2 to 0.4 wt% Cl, with slightly higher amounts of Cl in OP008.



Fig. 4. A-C - EMP analyses of Al, Mg, and Na in atoms per formula unit (p.f.u) in amphibole from the reaction rims plotted against Si. D - Cl ploted against K.



Fig. 5. EMP analyses of Al, Mg, and Na (p.f.u) in clinopyroxene from the reaction rims plotted against Si (p.f.u.).

All glasses have low totals (approx. 91%), reflecting a high volatile concentrations.

# 3.4. Line scans

Three EMP line scans were taken on samples OP001 (800 °C and no added fluid), OP005 (900 °C and no added fluid), and OP008 (900 °C and 2 wt% 2 mol NaCl fluid added) and are shown in Fig. 7. Chemical variations at the interfaces between the two phases are generally the result of mixed analyses. Gradual chemical variations through the reaction rims over several microns between the olivine-rim and plagioclase-rim interfaces indicate real chemical gradients across the rims. All three samples show strong chemical gradients across the reaction rims, particularly within amphibole. The diopside inner rim (towards the olivine-rim interface) in sample OP001 is relatively homogenous in composition compared with the outer (towards the plagioclase interface) amphibole rim. Amphibole shows increasing Al<sub>2</sub>O<sub>3</sub> and Na<sub>2</sub>O with decreasing FeO and MgO from the olivine interface towards the plagioclase interface. This follows expected compositional gradients

across the reaction rim with  $Al_2O_3$  and  $Na_2O$  originating from the plagioclase matrix and MgO and FeO originating from the olivine, although this is less clear in sample OP001. In samples OP005 and OP008, K<sub>2</sub>O and CaO have flat profiles across the amphibole rim. In sample OP001 there is a spike (up to 9 wt%) in K<sub>2</sub>O and a dip in CaO (<<1 wt%) at the amphibole-diopside interface that would be consistent with the presence of possible sub-micron phlogopite grains in this interface. Olivine in samples OP005 and OP008 are slightly depleted in FeO and enriched in MgO within 5–8 µm of the rim interface.

#### 4. Discussion

# 4.1. Diffusion limited reaction processes

The kinetics of reaction rim growth in these experiments are either controlled (rate limited) by interfacial processes (dissolution-precipitation) or by the diffusion rates of components across the reaction rim. For interface limited reactions, diffusion is highly efficient and rim growth is determined by the rates at which the reacting phases are consumed and



Fig. 6. EMP analyses of Al, Mg, and Na (p.f.u), and Cl in wt% in phlogopite from the reaction rims plotted against Si.



Fig. 7. Line scans across reaction rims. Sample OP001; 800 °C at 0.8 GPa and no fluid added, Sample OP008; 900 °C at 0.8 GPa and 2 wt% of 2 mol NaCl fluid added, Sample OP005; 900 °C at 0.8 GPa with no fluid added.

the product phases are precipitated at the reaction interfaces. The resulting product phases are therefore expected to be homogenous in composition. The line scans in Fig.7 show that this is not the case in these experiments. Therefore, diffusion was inefficient and most likely to be the rate-limiting process. Diffusion within the reaction rims tends to be concentrated along grain boundaries, as grain boundary diffusion coefficients are orders of magnitude greater than volume diffusion coefficients (Dohmen and Milke, 2010). Due to the relatively large temperature gradients across the capsules (40-50 °C) during peak experimental P-T, it is necessary to consider advection as a transport mechanism in the experiments if the fluid along grain boundaries is fully interconnected and has the physical properties (e.g. diffusion rates) of a free fluid. In other chemical systems (e.g. forsteriteenstatite-quartz), grain boundaries are understaturated in fluid at 0.05–0.1 wt% H<sub>2</sub>O. Above 0.1 wt% H<sub>2</sub>O, diffusivities indicate that two competing mechanisms dominate; diffusion in hydrous-saturated grain boundaries where fluid pores are isolated, and diffusion through fluid filled channels where pores are connected (Gardés et al., 2012; Milke et al., 2013). It is uncertain, in our experiments, if the grain boundary fluids became interconnected or at what fluid contents this could have happened. Given that the presence of isolated pores visible in the BSE images of the matrix plagioclase and rim phases for experiments with no added water and lower fluid contents (<2 wt% added fluid) (Fig. 2A-E), the presence of a transient porosity but not an interconnected fluid phase is most likely. Larger voids (Fig. 2F, G and I) in experiments with 2 wt% (e.g. OP008) added fluid seem to indicate the presence of an interconnected fluid phase such that advection could have been an important transport mechanism in these experiments.

#### 4.1.1. Effects of fluid on rim thicknesses and mineralogy

By changing the fluid composition and amounts, it is clear that both the reaction rim thicknesses and rim mineralogy can vary considerably (Table 3). Reaction rims generally increase with bulk fluid wt%, particularly for amphibole dominated rims. This indicates that increasing the fluid content increases the rates or extent of the reaction. Increasing the fluid rock ratios has been demonstrated in many other systems to significantly increase the reaction rates and rim growth (for example Carlson, 2010; Gardés et al., 2012; Milke et al., 2013; Rubie, 1986). A quantitative relationship between fluid content and rim thickness is, however, difficult to determine due to changes in mineralogy and grain size within the rims. For example, experiments in this study, with very high  $H_2O$  contents, typically had smaller rim grain sizes and higher amounts of porosity.

Drying at higher temperatures reduces the amount of fluid present within the starting materials and therefore during the experiments. We note a significant difference between samples that were dried at 200 °C and 100 °C, where the former shows no signs of reaction under BSE imaging. Our results are consistent with the experiments of Liu et al. (1997), who also showed that drying samples at higher temperatures decreased the rates of reaction rim growth. This highlights the significance that even small amounts of fluids (<< 1 wt% levels) can influence the formation and growth rates of reaction rims (Milke et al., 2013).

#### 4.2. Mass balance equations

Balanced equations can be derived to describe the mass transfer occurring across the reaction rims using a similar formulation to Ferry (1985). The reactions are compared for simple rims of amphibole only (OP003, OP005, OP007 and OP008) as this is the most common rim assemblage formed in our experiments and allows the possibility of comparing four different run experiments. The amphibole compositions are calculated using average rim compositions for each sample. The results are shown below in Eq. 1-4 (Table 5). The ratios of olivine to plagioclase consumed are between 1.1 and 1.3 for all four experiments. For experiments OP003, OP007, and OP008 the ratio of forsterite to favalite consumed is >0.96, compared to 0.91 in the starting San Carlos olivine, which means that the residual olivine should become enriched in the favalite component, however, the opposite is observed with Mg richer olivine at the rim interface (see Fig. 2). Therefore, the fluids must become enriched in Fe relative to Mg. For sample OP005 the ratio of forsterite to favalite consumed is 0.83 and this should cause depletion in Fe at the olivine-rim interface, which is observed in the line scans (Fig. 7). For all four experiments, the ratios of anorthite to albite consumed in the reaction are between 0.78 and 0.94, which are significantly higher than the starting matrix compositions of plagioclase. Enrichment in the albite content of the matrix plagioclase is therefore expected. However, due to the much large matrix volume relative to volume of rim phases formed, albite enrichment is not detected in analyses of matrix plagioclase. From the equations, approximately 2% of apatite is consumed, which is similar to the amounts of plagioclase (>96%) and apatite (2-3 wt%) within the original starting materials.

#### 4.3. Formation of symplectitic coronas in continental gabbros

Complex reaction rims composed of clinopyroxene, amphibole, and phlogopite were formed in these experiments. The most common olivine corona assemblages formed in nature, consisting of an inner shell of orthopyroxene at the olivine interface and an outer symplectitic shell

#### Table 5

Mass balanced reaction equations for samples OP003, OP005, OP007 and OP008 using average amphibole analyses for each sample.

- $\begin{array}{l} OP003 \; Eq.(1)\; 2.5 \; Mg_2SiO_4 + 1.8CaAl_2Si_2O_8 + 0.5NaAlSi_3O_8 + 0.04Ca_5(PO_4)_3Cl + \\ 2.7H_2O = [Ca_{0.9}Na_{0.1}][MgCa][AlMg_4](Al_{0.4}Si_{7.6}O_{22})(OH)_2 + 2.5OH^- + \\ 1.35Al_2O_3 \end{array}$
- $\begin{array}{l} \mathsf{OP005}\ \mathsf{Eq.}(2)\ 0.35\mathsf{Fe_2SiO_4}+1.75\mathsf{Mg_2SiO_4}+1.7\mathsf{CaAl_2Si_2O_8}+0.3\mathsf{NaAlSi_3O_8}+0.04\mathsf{Ca_5}(\mathsf{PO_4})_3\mathsf{Cl}+0.1\mathsf{SiO_2}+2\mathsf{H_2O}=[\mathsf{Ca}_{0.6}\mathsf{Na_{0.3}}][\mathsf{Mg}_{0.7}\mathsf{Ca_{1.3}}][\mathsf{Al_{1.5}Mg}_{2.8}\mathsf{Fe_{0.7}}]\\ (\mathsf{Al_{1.5}Si}_{6.5}\mathsf{O_{22}})(\mathsf{OH})_2+2\mathsf{OH}^-+0.3\mathsf{SAl_2O_3} \end{array}$
- $\begin{array}{l} \mathsf{OP007}\ \mathsf{Eq.}(3)\ 0.1\mathsf{Fe}_2\mathsf{SiO}_4 + 2.2\mathsf{Mg}_2\mathsf{SiO}_4 + 1.7\mathsf{CaAl}_2\mathsf{Si}_2\mathsf{O}_8 + 0.1\mathsf{NaAlSi}_3\mathsf{O}_8 + \\ 0.04\mathsf{Ca}_5(\mathsf{PO}_4)_3\mathsf{Cl} + 0.8\mathsf{SiO}_2 + 2.3\mathsf{H}_2\mathsf{O} = [\mathsf{Ca}_{0.9}\ \mathsf{Na}_{0.1}][\mathsf{MgCa}][\mathsf{Al}_{1.4}\mathsf{Mg}_{3.4}\mathsf{Fe}_{0.2}] \\ (\mathsf{Al}_{1.2}\mathsf{Si}_{6.8}\mathsf{O}_{22})(\mathsf{OH})_2 + 2.6\mathsf{OH}^- + 0.4\mathsf{SAl}_2\mathsf{O}_3 \end{array}$
- $\begin{array}{l} \mathsf{OP008} \ \mathsf{Eq.}(4) \ 0.1 \mathsf{Fe_2SiO_4} + 2.15 \mathsf{Mg_2SiO_4} + 1.7 \mathsf{CaAl_2Si_2O_8} + 0.25 \mathsf{NaAlSi_3O_8} + \\ 0.04 \mathsf{Ca_5}(\mathsf{PO_4})_3 \mathsf{Cl} + 0.2 \mathsf{SiO_2} + 2.1 \mathsf{H_2O} = [\mathsf{Ca}_{0.9} \ \mathsf{Na_{0.1}}] [\mathsf{MgCa}] [\mathsf{Al_{1.5}Mg_{3.3}Fe_{0.2}}] \\ (\mathsf{Al_{1.4}Si_{6.6}O_{22}}) (\mathsf{OH})_2 + 2.2 \mathsf{OH}^- + 0.45 \mathsf{Al_2O_3} \end{array}$

consisting of either clinopyroxene + spinel or amphibole + spinel at the plagioclase interface, (Table 1) were not replicated at 0.8 GPa and 800 to 900 °C for the fluid conditions present in our experiments. It is possible that natural coronas, which most likely require long (100's of years), multistage histories to form within gabbroic intrusions, cannot be easily replicated using piston cylinder experiments. Multistage formation has been suggested by Gallien et al. (2012) whereby there is an initial peritectic reaction to form orthopyroxene coronas, followed by amphibole + spinel symplectite formed at the expense of orthopyroxene coronas during cooling.

Our experiments are within the spinel + pyroxene phase field of several studies (Green and Ringwood, 1972; Irving and Green, 1970; Kushiro and Yoder Jr, 1966) and within the pressure estimates for most coronas in natural samples (see Table 1). As the pressures are lower than shown in some other studies (Emslie 1970; Herzberg 1970), it is possible that the experiments were conducted at pressures too low for the desired corona assemblage to form. Experiments at higher pressures of 1.8 GPa by Keller et al. (2008) produced rims of pyroxene and garnet (amongst other phases), suggesting that 1.8GPa is too high for spinel to be stable in the corona assemblage. The formation of orthopyroxene-spinel symplectites might therefore require higher pressures of between 0.8 and 1.8 GPa, which would suggest higher pressures than previously suggested for corona formation in natural samples.

Temperatures significantly above the solidus have not been explored here. The reaction between small amounts of interstitial melt and olivine-plagioclase aggregates has been suggested as a possible mechanism for forming coronas (De Haas et al., 2002; Gallien et al., 2012). Trapping of interstitial melt could be an alternative explanation for the apparent localization of corona development in some locations.

The fluid present in these experiments consisted of NaCl-bearing H<sub>2</sub>O. While the presence of NaCl would help to lower the H<sub>2</sub>O activity of the fluid, other volatiles, such as CO<sub>2</sub>, would also help to lower the H<sub>2</sub>O activity (Harlov, 2012; Newton et al., 1998; Newton and Manning, 2010; Yardley and Graham, 2002). This could affect the stability and abundance of amphibole and/or phlogopite during rim formation on the olivine grains. In contrast, fluid compositions from exposed sections of the lower crust tend to have even higher salt concentrations of X<sub>salt</sub> = 0.05–0.4 (Manning 2018; Markl and Bucher, 1998) compared to those in our experiments (X<sub>NaCl</sub> = 0–0.035).

### 4.4. Melt - fluid relationships

The dacite-trachydacite glass compositions formed at 900 °C in samples OP007 and OP008 were melts at peak experimental conditions. The glasses have broadly similar compositions with melts formed by hydrous partial melting of the gabbro (e.g. Koepke et al., 2004) at melt fractions of <10% (when the experimental data presented here are normalized to 100) except for much lower Fe since the bulk system chemistry of the experiments is Fe-poor. Melt fractions from these experiments are very low, i.e. <1 to 2%, which indicates that the wet solidus of the reactive system in these experiments was apparently just below 900 °C.

The low oxide wt% totals of the glasses measured in OP007 and OP008 (Table 4) indicate a high volatile content of potentially up 10 wt%. This is confirmed in part by the presence of large vesicles in the glass that are interpreted to have formed at peak experimental conditions, and not during quenching. This means that there was most likely a coexisting melt and fluid phase in OP007 and OP008. Using the reported  $K_DCI^{melt/fluid}$  of 0.077 at 0.75 GPa and 695 °C for a dacite melt composition from Kilinc and Burnham (1972), the estimated Cl composition of a coexisting fluid with the melt is 3.8 wt% for OP007 and 6.1 wt % for OP008, or ~ 1.1 and 1.7 mol Cl in the fluid, respectively. For OP008 this is close to or slightly lower than the original starting fluid composition of 2 mol NaCl.

# 4.5. Phlogopite formation

Our starting mixtures are generally low in K<sub>2</sub>O with negligible amounts in olivine and generally low amounts in matrix plagioclase (0.03–0.08 wt%; Table 2), moderate amounts in matrix amphibole (0.68–0.85 wt%; Table 2), and low amounts in matrix apatite (Table 2). However, phlogopite is a common and sometimes abundant reaction rim phase in the experiments. It is known that K is highly soluble, mostly as KCl, in high P-T crustal fluids (Aranovich and Newton, 1997; Markl et al., 1998) meaning that any  $K_2O$  in the sample materials (e.g. plagioclase or amphibole) will be soluble in the fluid phase, such that it can be transported to the reaction rim interface (by diffusion or potentially advection) and stabilize phlogopite. Secondly, whilst the matrix plagioclase contains relatively low amounts of K<sub>2</sub>O, it constitutes the vast majority of the mass of the experimental charge. Comparatively, the rim phlogopite is rich in K<sub>2</sub>O but is volumetrically small in the experimental charge. It is possible that some of the experiments contained matrix plagioclase that was more enriched in K<sub>2</sub>O than the average analyses given in Table 2. It is also possible that the matrix amphibole in the starting material is more common than actually observed after the experiments, as much of the amphibole broke down and crystallized as amphibole and co-existing phlogopite in the reaction rims. Despite a number of uncertainties (e.g the volume of olivine in the samples), we calculated the total amount of K<sub>2</sub>O in the original bulk sample and the total K<sub>2</sub>O within phlogopite formed in the experiments. The bulk K<sub>2</sub>O of the sample was calculated for sample OP001 using the average starting material compositions (Table 2). Due to the large percentage of plagioclase in the starting materials (>84 wt%) the estimated bulk K<sub>2</sub>O is 0.75 wt% (only slightly less than that of the average plagioclase). With a total sample weight of 0.0313 g, the total K<sub>2</sub>O in the bulk starting material is estimated to be 0.0015 g. The total K<sub>2</sub>O in the rims is calculated by determining the total mass of phlogopite formed in the reaction rims. The total mass of a 5 µm inner rim of phlogopite (from Fig. 7 the maximum inner phlogopite thickness is 5 µm) around a spherical grain of olivine with a diameter of  $375\,\mu m$  (median between 250 and 500 µm sieve sizes used in olivine fragment separation – see methods) is calculated to be  $1.8 \times 10^{-6}$  g. If the K<sub>2</sub>O in phlogopite is approximately 8 wt% (see Supplementary Table 3), the total K<sub>2</sub>O contained in the phlogopite rims would be approximately  $1.4 \times 10^{-7}$  g. The amount of K<sub>2</sub>O in the starting material is therefore over four orders of magnitude greater than the amount of K<sub>2</sub>O consumed by the formation of rim phlogopite. Despite large uncertainties in the total volume of olivine and therefore rim phlogopite, and the small amount of K<sub>2</sub>O within the rim amphibole, it is clear that the rim phlogopite could easily form without significantly depleting the matrix plagioclase in K<sub>2</sub>O during the experiments. The experiments do, however, demonstrate that only small amounts of K<sub>2</sub>O are required to stabilize phlogopite in the reaction rims.

#### 4.6. Formation of Cl-rich amphibole

Most of the amphiboles that formed in the experiments presented here contain <0.2 wt% Cl except for amphiboles from samples OP004 (0.34–0.65 wt% Cl), sample OP010 (0.4–1.45 wt% Cl), and sample OP005 (most at 0.15–0.17 but one with 0.83 wt% Cl). Several studies of naturally formed amphibole show that Fe-rich amphiboles contain higher Cl contents than Mg-rich amphiboles (e.g. Enami et al., 1992; Leger et al., 1996; Liu et al., 2009; Vanko, 1986; Xiao et al., 2005), which implies that there are crystal chemical controls on the incorporation of Cl into amphibole with increasing Na + K and Fe. This is also observed in natural amphibole as well as in biotite (Vanko, 1986, Leger et al., 1996; McCormick and McDonald, 1999; Kullerud et al. 1999; Coogan et al., 2001; Gillis and Meyer, 2001; Liu et al., 2009). Alternatively, increasing NaCl in the fluid can lead to Fe-richer amphibole compositions (Khodorevskaya and Aranovich 2016). The Cl contents (0.34–0.65 wt%) in amphiboles from Sample OP004 (800 °C and 2 wt% NaCl fluid added) are significantly higher than the Cl contents in amphiboles (below detection limits to 0.09 wt%) from OP007 (900 °C and 2 wt% fluid added) and OP008 (900 °C and 2 wt% NaCl fluid added). This could be related to the presence of melt in OP007 and OP008 but not in OP004. As shown above, the estimated Cl contents of fluids in equilibrium with the melts in OP008 would have a Cl content (1.7 mol) similar to that of the original added fluid (2 mol NaCl). Samples OP007 and OP008 have  $X_{Mg} > 0.94$ , whereas the amphiboles in OP004 have an  $X_{Mg}$  of 0.7. The higher Cl contents in the amphibole relative to those from OP007 and OP008.

It has also been shown that H<sub>2</sub>O becomes locally consumed during the formation of the hydrous phases thereby raising the concentration of Cl in the residual fluid and the Cl concentrations in amphiboles (Kullerud et al., 2001; Liu et al., 2009; Markl et al., 1998). Furthermore, the experimental data of Chan et al. (2016) showed that amphiboles have low Cl contents (<0.4 wt%) over a large range in NaCl molality until halite saturation is reached (83 mol NaCl or XNaCl = 0.6). Due to the small volume of rim phases formed in the reaction relative to the volume of the bulk starting materials, the amount of H<sub>2</sub>O in samples with 0.05 wt% (OP002 and OP005) will be approximately 2-3 orders of magnitude greater than the amount of H<sub>2</sub>O within the rim amphibole. It is unlikely that fluid is being significantly consumed during the reaction in samples with fluid added. In dried samples, the exact fluid amounts are unknown and it is possible that the very low fluid contents are indeed (partially) consumed during the reaction in samples OP001 and OOP005. The Cl content of rim amphibole in sample OP005 varies significantly from 0.15 to 0.83 wt% Cl. The large variations in Cl in amphibole from OP005 may therefore indicate local variations in fluid Cl contents, which arose from isolated and transient fluid pores that locally or temporally become depleted in H<sub>2</sub>O and enriched in Cl as amphibole forms.

The large difference in pressure between oceanic gabbros and the experiments from this study or continental gabbros show that the Cl content of the amphiboles is mostly dependent on the chemistry  $(X_{Mg})$  of the amphibole or the presence of localized enrichment in Cl in pore fluids along grain boundaries. Amphiboles formed in our experiments tend to be richer in Al<sub>2</sub>O<sub>3</sub> compared to those observed in secondary rims and veins from oceanic crust (e.g. Gillis and Meyer, 2001) but more closely comparable to those from lower continental crust (e.g. De Haas et al., 2002). It is possible that the higher Al contents in our samples are related to the higher solubility of Al in fluids with increasing pressure as well as increasing Si and alkalis (Manning, 2007; Tropper and Manning, 2007), although this is difficult to determine without data from a wider range of pressures with the same bulk compositions as those used here.

#### 5. Conclusions

In all of our experiments, except for sample OP009 (at 0.8 GPa, 800 °C and no fluid added), the olivine single grains and plagioclase matrix reacted to form coronas. The coronas consisted of clinopyroxene, clinopyroxene + amphibole, and clinopyroxene + phlogopite. However, under the experimental conditions used here, coronas of orthopyroxene + clinopyroxene or amphibole + spinel, that are commonly found in natural samples of metamorphosed gabbros from the mid-lower continental crust, were not reproduced. The coronas formed in natural gabbro samples could be the result of a more complicated metamorphic history, and/or by the presence of small amounts of melt (De Haas et al., 2002; Gallien et al., 2012). Pressure differences between the oceanic crust and the continental crust are evident in the amphibole chemistry. This is partly related to solubility differences for various elements (e.g. Al) at higher pressures. However, we also note that local variations in the fluid composition during reaction will also affect the composition of secondary amphibole. Several key results from the experiments can be applied to reactions between gabbroic rocks and NaCl-rich fluids for both continental and oceanic crust;

- 1 Reaction rates increase with increasing amounts of fluid present in the samples, meaning that reaction rates are dependent on the level of fluid saturation along grain boundaries and interphase boundaries. This is in keeping with a large amount of data within other experimental metamorphic systems (Carlson, 2010; Gardés et al., 2012; Milke et al., 2013; Rubie, 1986).
- 2 Reactions rates are also significantly increased with increasing concentrations of NaCl in the fluid, highlighting the role of halogens and brines in reaction rim forming processes in the lower crust.
- 3 The near solidus temperature of the reactive system is at 900 °C with 2 wt% added fluid. The melt compositions formed had dacite-trachyte compositions and likely contained significant amounts of H<sub>2</sub>O and Cl. These melts have similar compositions to experimentally and naturally produced plagiogranites formed by wet partial melting of gabbro in the oceanic crust at 0.2 GPa (Koepke et al., 2004). Our experiments therefore straddle the hydrothermal-magmatic divide.
- 4 The high Cl contents (up to 0.83 wt%) in the secondary rim amphiboles may have been related to localized enrichments in Cl in the neighboring pore fluids due to consumption of  $H_2O$  during the formation of hydrous phases. This would also have been supported by a strong positive correlation between the FeO and Cl contents in the amphiboles.

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#### Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi. org/10.1016/j.lithos.2018.07.013.

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