On the origin of multi-layer coronas between olivine and plagioclase at the gabbro–granulite transition, Valle Fértel–La Huerta Ranges, San Juan Province, Argentina

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ABSTRACT
Troctolitic gabbros from Valle Fértel and La Huerta Ranges, San Juan Province, NW-Argentina exhibit multi-layer corona textures between cumulus olivine and plagioclase. The corona mineral sequence, which varies in the total thickness from 0.5 to 1 mm, comprises either an anhydrous corona type I with olivine|orthopyroxene|clinopyroxene+spinel symplectite|plagioclase or a hydrous corona type II with olivine|orthopyroxene|amphibole|amphibole+spinel symplectite|plagioclase. The anhydrous corona type I formed by metamorphic replacement of primary olivine and plagioclase, in the absence of any fluid/melt phase at <840 °C. Diffusion controlled metamorphic solid-state replacement is mainly governed by the chemical potential gradients at the interface of reactant olivine and plagioclase and orthopyroxene and plagioclase. Thus, the thermodynamic incompatibility of the reactant minerals at the gabbro–granulite transition and the phase equilibria of the coronitic assemblage during subsequent cooling were modeled using quantitative MgO–CaO phase diagrams. Mineral reaction textures of the anhydrous corona type I indicate an inward migration of orthopyroxene on the expense of olivine, while clinopyroxene+spinel symplectite grows outward to replace plagioclase. Mineral textures of the hydrous corona type II indicate the presence of an interstitial liquid trapped between cumulus olivine and plagioclase that reacts with olivine to produce a rim of peritectic orthopyroxene around olivine. Two amphibole types are distinguished: an inclusion free, brownish amphibole I is enriched in trace elements and REEs relative to green amphibole II. Amphibole I evolves from an intercumulus liquid between peritectic orthopyroxene and plagioclase. Discrete layers of green amphibole II occur as inclusion-free rims and amphibole II+spinel symplectites. Mineral textures and geochemical patterns indicate a metamorphic origin for amphibole II, where orthopyroxene was replaced to form an inner inclusion-free amphibole II layer, while clinopyroxene and plagioclase were replaced to form an outer amphibole+spinel symplectite layer, at <770 °C. Calculation of the possible net reactions by considering NCKFMASH components indicates that the layer bulk composition cannot be modeled as a ‘closed’ system although in all cases the gain and loss of elements within the multi-layer coronas (except H2O, Na2O) is very small and the main uncertainties may arise from slight chemical zoning of the respective minerals. Local oxidizing conditions led to the formation of orthopyroxene+magnetite symplectite enveloping and/or replacing olivine. The sequence of corona reaction textures indicates a counter clockwise P–T path at the gabbro–granulite transition at 5–6.5 kbar and temperatures below 900 °C.

Key words: Argentina; metagabbro; multi-layer corona; olivine–plagioclase contact; Valle Fértel–La Huerta Ranges.

INTRODUCTION
There are many different types of reaction structures that may occur in various lithologies that now separate thermodynamically incompatible mineral assemblages (Thompson, 1959; Joesten, 1974, 1977, 1986; Ashworth, 1986a; Clarke & Powell, 1991; Markl et al., 1998; Abart et al., 2001; Cruciani et al., 2008; White et al., 2008). Following on from these earlier studies it is clear that any model of the origin of such structures has to comply with the following requirements: (i) the juxtaposed thermodynamically incompatible mineral assemblages are physically separated by reaction structures and, (ii) the minerals comprising the reaction structures are compatible with the original minerals of the host rock within a specific mineral facies.
These structures have yielded important information about both the P–T evolution of the rocks including the tectonic significance of their occurrence regionally and the metamorphic processes that form these structures. However, the duration of changing P–T conditions was too transient for the reactions to reach completion although there was enough time for the reaction to commence. As a result the most obvious feature of layered reaction structures is the sharp discontinuity in the mineral modes from layer to layer and hence in the bulk composition of each layer. The minerals in the core of coronas and in the matrix outside the reaction structures are interpreted as preserved relics of a primary paragenesis once in thermodynamic equilibrium. The preservation of such corona textures is often ascribed to rapid reaction progress at relatively dry conditions, and little or no recrystallization and deformation follows their formation, otherwise they would be destroyed (Wayte et al., 1989; Lang & Gilotti, 2001). Joesten (1986) suggested a magmatic (pre-metamorphic) origin for orthopyroxene coronas around olivine separating it from plagioclase followed by a subsequent metamorphic annealing leading to the formation of intervening amphibole + spinel symplectite layers. However, in contrast Ashworth (1986a) ascribed such coronas to a metamorphic replacement of plagioclase and adjacent olivine.

As coronic and symplectic microstructures do not reflect the whole-rock chemical composition, the steady-state diffusion model of Joesten (1977) turned out to be an efficient approach to derive component diffusivities within transport controlled reaction corona textures. The model assumes a ‘closed’ system, except for H₂O, and that all mineral layers of a multi-layer corona already exist with infinitesimal thickness at incipient corona formation, so that the internal mineral sequence remains unchanged during layer growth. The steady diffusion model was applied in particular to multi-layer coronas between olivine and plagioclase in high-grade metagabbros by Mongkoltip & Ashworth (1983), Joesten (1986), Ashworth & Sheplev (1997), Lang et al. (2004). This study was carried out in the Valle Fértil and La Huerta Range, San Juan Province, NW-Argentina (Fig. 1), and focuses on troctolitic gabbros that exhibit multi-layer coronas between olivine and plagioclase. The reaction coronas between previously bordering minerals (here olivine and plagioclase) involve the (partial) consumption of the reactant minerals and the growth of new minerals between them. The products are arranged in layers showing a typical sequence of corona type I olivine|orthopyroxene|clinopyroxene + spinel symplectite|plagioclase. Corona type I evolves into corona type II upon cooling to form the mineral sequence olivine|orthopyroxene|amphibole|amphibole + spinel symplectite|plagioclase. In some cases orthopyroxene + magnetite symplectite is formed adjacent to olivine as also documented elsewhere. Such microstructures are often ascribed to changing P–T conditions and mass transfer between olivine and plagioclase during metamorphism (Mongkoltip & Ashworth, 1983; de Haas et al., 2002), as first described by Törnebohm (1959). Based on petrographic observations (Figs 2a–e, 3 & 6a,b), the qualitative reactions (1) and (2) can be written, neglecting possible gains and losses of components:

\[ \text{Ol} + \text{Pl} = \text{Opx} + \text{Cpx} + \text{Spl}; \]  
\[ \text{Opx} + \text{Pl} + \text{H}_2\text{O} = \text{Am} + \text{Spl}. \]  

This study emphasizes a combined magmatic and metamorphic origin for these multi-mineral layers. However, in both cases, the textural development of these coronas is controlled by diffusion within a reaction zone (White et al., 2008). Trace element and REE patterns across selected coronas shed light on the behaviour of these elements within each mineral layer. The new data provide evidence for a magmatic origin for some parts of the corona where the contribution of an interstitial melt may have played an important role and may have led to the formation of peritectic orthopyroxene and interstitial pargasitic amphibole, the latter enriched in trace elements and REEs. Other parts of the corona are consistent with solid-state replacement of plagioclase and adjacent olivine at

![Simplified geological map of the Valle Fértil–La Huerta Ranges](image-url)
Fig. 2. Backscattered electron (BSE) images and thin section photomicrographs of representative corona structures. (a) The corona assemblage around olivine comprises orthopyroxene/amphibole/amphibole + spinel in sample J7205. Plane polarized light (PPL). (b) An olivine megacryst separated by a multilayer corona from adjacent matrix plagioclase. A thin orthopyroxene–magnetite layer locally forms the inner shell adjacent to olivine, followed by an orthopyroxene–spinel layer. Locally a pure orthopyroxene layer is formed between olivine and the orthopyroxene–spinel layer. The continuous amphibole + spinel and discontinuous clinopyroxene + spinel rim forms the outer part of the corona. Fine grained, elongated, divergent spinel rods in clinopyroxene are perpendicular to the layer sequence, while the spinel rods in amphibole are shorter in elongation and less well oriented. (c) Sketch of the BSE-image shown in (b). The layer widths are drawn to scale, except the widths of spinel rods and magnetite which are exaggerated. (d) The centre part of the corona consists of orthopyroxene + magnetite symplectite in a leuco-gabbro. A continuous orthopyroxene layer of nearly constant width is formed around the oxidized centre. (e) Detail BSE-image of a multi-layer corona separating olivine from matrix plagioclase in a leuco-gabbro. The columnar orthopyroxene layer is of almost constant width and grows perpendicular to the olivine contact. A spinel-free amphibole layer is developed between orthopyroxene and the outer shell of amphibole + spinel symplectite. (f) Coarse-grained clinopyroxene is mantled by an amphibole rim in a leuco-gabbro and exhibits parallel exsolution lamellae of magnetite and chrome-rich spinel. Orthopyroxene exsolution lamellae are oriented ∼ perpendicular to the magnetite and chromite.
post-magmatic (granulite facies) conditions. The interpretation that these coronas formed by magmatic followed by metamorphic processes strengthens the geodynamic model of a back arc and deep arc in the San Juan Province, where the magmatic activity led to granulite facies metamorphism in the crystalline basement in the Early Ordovician (Pankhurst et al., 1998; Gallien et al., 2010).

REGIONAL GEOLOGY AND FIELD RELATIONS

The Sierras of La Huerta–Valle Fértil (Fig. 1) are part of the Sierras Pampeanas tectono-stratigraphic province, which include the Upper Proterozoic and Lower Palaeozoic metamorphic and igneous rocks of Central and NW-Argentina. They belong to the Western Pampean Ranges, which are considered the key to understanding the connection between the Pampean and Laurentian terranes in the western margin of Gondwana (Caminos, 1979; Ramos et al., 1996; Thomas & Astini, 1996; Pankhurst et al., 1998). Several models have been proposed regarding the evolution of this area, which include a Western Pacific arc type margin (Palaeo- to Mesoproterozoic), evolving to a passive margin in the Neoproterozoic and subsequent reestablishment of a magmatic arc (Proterozoic–Cambrian boundary, Pampean cycle). This evolution continued with the development of an Andean-type margin in the Lower Palaeozoic (Famatinian cycle) and ended in the Ordovician with the collision of the Precordillera. The present topography is suggested to be a result of Neogene tectonics (Pankhurst et al., 1998). Two belts are recognized within the basement of the Sierra de Valle Fértil–La Huerta (Pankhurst et al., 1998): (i) an eastern belt comprising gabbric, dioritic and tonalitic meta-intrusive rocks, granodiorites, pegmatites and aplites; and (ii) a western belt comprising garnet–sillimanite–cordierite gneisses and amphibolites.

The gabbric rocks from Valle Fértil and La Huerta are irregular shaped bodies of up to several kilometres in length and width, surrounded by migmatitic gneisses. The gabbric rocks intruded the Proterozoic metasedimentary crystalline basement during the Late Cambrian to Early Ordovician (Pankhurst et al., 1998; Rapela, 2000; Gallien et al., 2010). They are considered to be the heat source for the granulite facies event that led to the migmatization of the country rocks (Otamendi et al., 2008; Gallien et al., 2009, 2010). Gabbric contacts with the gneisses and sometimes with the metacarbonates are typically tectonic, following NNE–SSW ductile shear zones (Delpino et al., 2008). Mylonitic bands stretching NNE–SSW and NNW–SSE crosscut the outcrops. In general, the gabbric bodies, even though they are locally deformed, still preserve the original igneous structure and texture. Igneous layering measuring a few centimetres in thickness can be recognized in a few cases as alternating bands in which the modal proportions of plagioclase to mafic minerals (olivine and pyroxene) vary (Mogessie et al., 2007). CIPW-normative minerals were calculated for the investigated coronitic gabbros, with Fe3+/FeTot set to 0.1 (Table 1). All analysed gabbric rocks are olivine normative but lack any feldspathoids, therefore they are subalkaline, but

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* Liq. temp. (°C) 1243 1294 1358

Table 1. Representative bulk rock chemical compositions of the metagabbros.

Trace elements ppm Chondrite normalizationb ppm Chondrite normalizationb ppm Chondrite normalizationb

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CIPW-Norm: Fe2+/FeTot = 0.1

LOI, loss on ignition.

a Liq. temp. (°C) was calculated by using the program "PELE" version 7.01 (Boudreau, 1999).

b Chondrite normalization (sample/chondrite) was done by using the data set of Nakamura (1974).

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silica saturated. The normative plagioclase content varies between 40 and 76 vol.%. Some samples contain <5 vol.% normative pyroxene and are classified as troctolites. The other samples vary in the orthopyroxene to clinopyroxene ratio and are classified as gabbros to norites or olivine gabbros to olivine norites. Major elements (in wt%), trace elements and REE concentrations (ppm) and chondrite normalized REE data are listed in Table 1. For chondrite normalization (sample/chondrite) the data set of Nakamura (1974) was used. The majority of the normalized values lie between 0.94 and 5.69, with a slight enrichment of the light REEs relative to the heavy REEs.

Peak metamorphic conditions of 850 °C and 6–7 kbar followed by isobaric cooling to 700 °C have been determined in associated migmatitic gneisses (Delpino et al., 2008; Otamendi et al., 2008; Gallien et al., 2010) and impure marbles (Gallien et al., 2009 and references therein). Cadmium-bearing lead–zinc mineralization occurs at the contact between the metamorphic gneisses and associated mafic meta-intrusive rocks (Mogessie et al., 2009).

METHODS

Minerals were analysed on carbon-coated polished thin sections at the Institute of Earth Sciences, Karl-Franzens-University of Graz, with a JEOL-6310 SEM equipped with a LINK ISIS energy dispersive system (EDS) and a MICROSPEC wavelength dispersive system (WDS). Analytical conditions were 15 kV accelerating voltage, 5 nA probe current and 5 μm beam diameter for silicates. Matrix corrections were made using the Phi–Roh–Z procedure. The following mineral standards were used: Si, K, Al – adularia; Fe, Mg – garnet or olivine; Ca, Ti – titanite; Mn – rhodonite; Zn – gahnite; Cr – synthetic Mg-chromite; Na – jadeite; Fe – F-phlogopite. The detection limits are 0.05 wt% for the WDS (Na–F), and 0.1–0.2 wt% for the EDS (for the rest of the elements analysed). Ferric iron was calculated based on the assumption of stoichiometry (Droop, 1987), which certainly imposes a limitation in interpreting small variations in ferric iron content. Major and trace elements of representative whole-rock samples have been analysed with a Bruker Pioneer S4 X wavelength dispersive XRF spectrometer at the Institute of Earth Sciences, Karl-Franzens-University of Graz and by ICP–MS at the Institute of Chemistry, Karl-Franzens-University of Graz. Samples were prepared as fused pellets using Li2B4O7 flux. In situ trace element and REEs were determined by LA–ICP–MS (New Wave UP 213 and Agilent 7500, Institute of Chemistry, KFU). The standard glass NIST610 was used for standardization and the software GLITTER for data reduction. SiO2 was used as internal standard. NIST612 and BCR2 glasses were routinely analysed as control standards and could be reproduced within 10%. Pit size was 40 μm. Mineral abbreviations are after Kretz (1983) and extended by Am = amphibole.

THE ORIGIN OF MULTI-LAYER CORONAS

Corona textures between olivine and plagioclase are especially well developed in plagioclase-rich gabbroic rocks. In general, the coronas are composed of an inner shell of radial columnar or fan-shaped inclusion-free orthopyroxene layer, or subordinate orthopyroxene+spinel and orthopyroxene+magnetite symplectite adjacent to plagioclase (Fig. 2a–e). In all observed coronas, the shape of each described layer parallels the shape of the olivine in the centre.

The width of the inner orthopyroxene shell ranges from few μm to 300 μm. The contact with olivine is gently undulating and tends to be convex towards olivine. The outer contact with amphibole tends to be more irregular. In a few cases, the orthopyroxene layer is missing and is replaced by an amphibole layer (Fig. 2b,c, upper left and lower right corner of the image). However, single, rounded orthopyroxene inclusions may occur within this amphibole corona (Fig. 6a). Discontinuous orthopyroxene + magnetite and orthopyroxene + spinel symplectite also occurs at the contact with olivine (Figs 2a–c & 7a). However, the three different orthopyroxene-bearing layers are rarely observed together within one corona.

The outer shell has a width of up to 900 μm and generally comprises an inner inclusion free and optically continuous amphibole layer adjacent to orthopyroxene, while the outer layer adjacent to plagioclase usually consists of coarse-grained amphibole+spinel symplectite rods (Figs 2a–e, 3 & 6a,b). In a few cases a discontinuous layer of clinopyroxene hosting fine grained, fan-shaped spinel symplectite rods oriented perpendicular to the layer contact occurs (Figs 2b,c & 7a). The inclusion-free amphibole sublayer facing towards orthopyroxene shows a sharp boundary with the amphibole+spinel symplectite (Figs 2d,e, 3 & 6a). The amphibole+spinel symplectite commonly consist of aggregates of tschermakite/pargasite, hosting elongated rods of spinel approximately perpendicular to the layer contact (Fig. 2a,d,e). Parallel oriented spinel rods in amphibole are significantly larger than spinel rods within clinopyroxene (Figs 2b,c & 6a). Locally, the amphibole+spinel and clinopyroxene+spinel layers are missing and orthopyroxene is the only layer present (Fig. 2b,c).

Relict igneous textures are in most cases well preserved and are indicative of a cumulate origin. Igneous minerals comprise coarse-grained laths of plagioclase, olivine and widely varying proportions of coarse-grained orthopyroxene and clinopyroxene. Olivine is commonly serpentinized. Igneous clinopyroxene contains abundant exsolution lamellae of orthopyroxene, chromite-spinel and magnetite and is often mantled by pargasitic amphibole. Chromite-spinel and magnetite have formed parallel to the same crystallographic
orientation and cross the orthopyroxene lamellae at an acute angle of \( \sim 75^\circ \) [this might be due to the cutting effect subparallel to the crystallographic plane (001); Fig. 2f].

Beside primary magmatic olivine, orthopyroxene+magnetite symplectites form the core of the corona (Fig. 2d). The primary reactant phase in the centre of the coronas also gets completely altered to iron hydroxides during late stage hydration (Fig. 6a).

**MAJOR ELEMENT MINERAL CHEMISTRY OF PRIMARY MINERALS**

Representative mineral compositions of the primary minerals are listed in Table 2. The relict igneous olivine is forsterite-rich with \( X_{\text{Mg}} \) ranging from 0.76 to 0.81 (\( X_{\text{Mg}} = \text{Mg}/(\text{Mg} + \text{Fe}^{2+}) \)), but individual grains are homogeneous. Plagioclase shows no chemical zoning and varies in composition from An_{95} to An_{99}. Igneous green spinel occurs as blocky inclusions in plagioclase; it is essentially a spinel–hercynite solid solution with an \( X_{\text{Mg}} = 0.54-0.66 \) and \( \text{Fe}^{3+} \leq 0.11 \) a.p.f.u. \( \text{Cr}_2\text{O}_3 \) ranges between 3.74 and 4.93 wt% in sample J7205, but spinel from J0105 is lacking \( \text{Cr}_2\text{O}_3 \). Cumulate clinopyroxene (Di_{75-76}) is a diopside–hedenbergite solid solution with \( X_{\text{Mg}} = 0.85-0.86 \) and \( \text{Al}_2\text{O}_3 = 3.34-4.09 \) wt%. Orthopyroxene occurs as an intercumulus phase between olivine and plagioclase and is mainly enstatite (En_{72-74}) with \( X_{\text{Mg}} \) of 0.77–0.78, a low \( \text{TiO}_2 \) content (<0.20 wt%) and \( \text{Al}_2\text{O}_3 \) of 2.04–2.71 wt%.

**MAJOR ELEMENT MINERAL CHEMISTRY OF THE CORONA MINERALS**

Representative chemical analyses of corona-forming minerals are summarized in Tables 3 & 4. Individual corona minerals do not show any significant chemical zoning in major elements. Corona-forming orthopyroxene (En_{71-78}) shows a slightly varying \( X_{\text{Mg}} \) of 0.77–0.81, which is within the same range as the relict primary orthopyroxene and olivine. The \( \text{Al}_2\text{O}_3 \) content of corona orthopyroxene is 1.80–2.47 wt%, which is slightly lower than the \( \text{Al}_2\text{O}_3 \) content of primary orthopyroxene. The chemical composition of Mg-spinel is very similar to the primary spinel. Symplectite spinel is free of \( \text{Cr}_2\text{O}_3 \), \( \text{Fe}^{3+} <0.10 \) a.p.f.u. and \( X_{\text{Mg}} \) lies between 0.59 and 0.64. The \( \text{Al}_2\text{O}_3 \) content of clinopyroxene (Di_{74-78}) is 2.08–3.95 wt% and \( X_{\text{Mg}} = 0.85-0.86 \). There is no significant difference in the major element composition of amphibole between the optically homogeneous, inclusion-free amphibole layer and the amphibole+spinel symplectite layer. After the IMA–Amphibole classification scheme (Mogessie et al., 2004) amphibole is a tschermakite–pargasite solid solution with \( \text{Al}^{3+} \) ranging from 1.48 to 1.71 and (\( \text{Na} + \text{K} \))_{\text{Total}} = 0.50–0.66 a.p.f.u and \( X_{\text{Mg}} \) is slightly varying between 0.79 and 0.85.

**TRACE ELEMENT AND REE CHARACTERISTICS OF PRIMARY AND CORONA MINERALS**

As major element compositions do not show any variations within the coronitic rims towards the con
tact to the neighbouring reactant mineral a detailed in situ LA–ICP–MS study was done (Tables 5 & 6) to evaluate the behaviour of trace elements and REEs within the coronitic assemblage in sample J0105. These data place constraints on the origin and formation history of the coronitic assemblage. Olivine and plagioclase are clearly of magmatic origin. However, part of the orthopyroxene and amphibole might have formed either by reaction of olivine with a residual liquid or by a metamorphic reaction at the expense of olivine, plagioclase and/or one of the corona minerals. Profile 1 was obtained within the amphibole layer in order to determine the possible magmatic r. metamorphic origin of the amphibole (Figs 3 & 4). Profile 2 (Figs 3 & 5a–f) reveals a slight outward increase towards the orthopyroxene–amphibole boundary in the concentrations of Ni, Cr, Ti, V and Ga. The concentration of Zn in orthopyroxene is higher than in amphibole and shows an inward increase towards the orthopyroxene–olivine boundary.

**Olivine** is the main host of divalent Ni and Zn, which have atomic radii close to Mg (Shannon, 1976). The Ni and Zn content ranges from 766 to 816 ppm and 30.8 to 32.8 ppm, respectively (Table 5). Ti ranges from 9.73 to 23.7 ppm. Other trace elements are incompatible and are usually below the detection limit.

**Plagioclase** (Figs 5a–f & 6c–h) is enriched in Ga and Sr, relative to amphibole and in Ba, La, Ce and Eu relative to orthopyroxene in sample J0105 (Table 5). Olivine and plagioclase show no consistent zoning between core and rim.

**Orthopyroxene** contains Ti concentrations of 224–298 ppm and V concentration of 14.5–29.7 ppm (Table 5). Profile 2 (Figs 3 & 5a–f) reveals a slight outward increase towards the orthopyroxene–amphibole boundary in the concentrations of Ni, Cr, Ti, V and Ga. The concentration of Zn in orthopyroxene is higher than in amphibole and shows an inward increase towards the orthopyroxene–olivine boundary.

**Amphibole** is enriched in most of the analysed elements, relative to olivine, orthopyroxene and plagioclase (Table 6). Only Ga and Sr, which substitute Al and Ca, have higher concentrations in plagioclase. Zn is enriched in orthopyroxene and olivine and Ni is concentrated in olivine, relative to amphibole. The trace element and REE signatures reveal two different amphibole types in sample J0105 (Figs 3 & 4a–d). The first amphibole (Am I) is enriched in all analysed elements.
Table 4. Representative chemical compositions of pargasitic corona amphibole (Prg = pargasite), Am I and Am II of sample J0105.

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Sample</th>
<th>Am(I)</th>
<th>Am(II)</th>
<th>Prg</th>
<th>Prg</th>
<th>Prg</th>
<th>Prg</th>
<th>Prg</th>
<th>Prg</th>
<th>Prg</th>
<th>Prg</th>
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<th>Prg</th>
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<tbody>
<tr>
<td>SiO2</td>
<td>J7205</td>
<td>44.5</td>
<td>45.0</td>
<td>45.0</td>
<td>44.6</td>
<td>45.2</td>
<td>43.4</td>
<td>44.4</td>
<td>43.2</td>
<td>43.1</td>
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<td>TiO2</td>
<td>J7205</td>
<td>0.86</td>
<td>0.46</td>
<td>&lt;0.1</td>
<td>0.10</td>
<td>1.67</td>
<td>2.06</td>
<td>2.00</td>
<td>1.91</td>
<td>1.73</td>
<td>0.47</td>
<td>0.65</td>
<td>0.62</td>
<td>0.78</td>
<td>0.83</td>
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<td>Al2O3</td>
<td>J0105</td>
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<td>13.4</td>
<td>13.8</td>
<td>14.7</td>
<td>11.8</td>
<td>13.3</td>
<td>12.2</td>
<td>13.9</td>
<td>13.7</td>
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<td>CaO</td>
<td>J0105</td>
<td>0.34</td>
<td>0.11</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
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<tr>
<td>Fe2O3</td>
<td>J0105</td>
<td>2.75</td>
<td>2.68</td>
<td>2.61</td>
<td>2.08</td>
<td>0.04</td>
<td>0.00</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>0.45</td>
<td>1.52</td>
<td>1.73</td>
<td>2.63</td>
<td>1.10</td>
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<tr>
<td>Na2O</td>
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<td>5.52</td>
<td>6.49</td>
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<td>6.92</td>
<td>7.5</td>
<td>7.13</td>
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<td>16.8</td>
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<td>16.8</td>
<td>16.0</td>
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<td>J0105</td>
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<td>12.5</td>
<td>11.9</td>
<td>12.0</td>
<td>11.8</td>
<td>12.0</td>
<td>11.9</td>
<td>12.3</td>
<td>12.1</td>
<td>10.2</td>
<td>12.0</td>
<td>10.1</td>
<td>12.0</td>
<td>12.0</td>
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<td>J0105</td>
<td>1.81</td>
<td>1.69</td>
<td>1.96</td>
<td>1.82</td>
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<td>1.50</td>
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<tr>
<td>TiO2</td>
<td>J0105</td>
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<td>0.20</td>
<td>0.12</td>
<td>0.15</td>
<td>1.1</td>
<td>1.13</td>
<td>1.14</td>
<td>0.96</td>
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<td>0.6</td>
<td>0.48</td>
<td>0.49</td>
<td>0.48</td>
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<tr>
<td>FeO</td>
<td>J0105</td>
<td>0.36</td>
<td>0.31</td>
<td>0.11</td>
<td>0.18</td>
<td>0.14</td>
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<td>0.17</td>
<td>0.11</td>
<td>0.21</td>
<td>0.29</td>
<td>0.36</td>
<td>0.20</td>
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<tr>
<td>H2O</td>
<td>J0105</td>
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<td>2.10</td>
<td>2.10</td>
<td>1.99</td>
<td>1.98</td>
<td>1.91</td>
<td>1.99</td>
<td>1.96</td>
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<td>100.5</td>
<td>99.0</td>
<td>98.9</td>
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</tr>
</tbody>
</table>

Elements, hosts no spinel and has a brownish colour, which is characteristic for Ti-rich amphibole. The other amphibole (Am II) is pale green and is significantly depleted in the trace elements and REE by about one order of magnitude relative to Am I (Fig. 4a–d). The major element concentrations show only slight differences between the two amphibole types (Table 4). At the beginning of profile (1) Am I forms an up to several millimetre wide convex embedding towards the centre of olivine and gets thinner along the profile (Figs 3 & 4a–d). The inclusion free, pale green amphibole layer (Am II) contains the lowest concentration of trace elements and REEs among amphibole (points 8–13 in Fig. 4a–d). To avoid mixed analyses of amphibole + spinel symplectite, only a few representative laser ablation spots were set in the narrow Am II layer. A decrease in the element concentrations from Am I to Am II is observed for all analysed elements and is clearly observed at points 7, 8 and 9. Towards the end of profile (1) (points 14–15–16), a more gentle increase in element concentration is observed (Fig. 4a–d). The major element concentrations show about one order of magnitude relative to Am I part of the amphibole layer towards plagioclase. The behaviour of Ni in amphibole is similar to Cr with an inward increase from 208 to 294 ppm at the amphibole–orthopyroxene boundary. A minor outward increase in V, Ti and Ga is obtained within the orthopyroxene layer, while all other elements tend to be rather homogeneous within each mineral layer.

PHASE EQUILIBRIA CONSTRAINTS

The metamorphic corona reactions

Using the constraint of Al and Si immobility within the corona, it is possible to determine the proportions of the reactant phases that produced the multi-layer corona of orthopyroxene/amphibole/amphibole + spinel and orthopyroxene/clinopyroxene + spinel in these samples. The reaction coefficients and volumes of the participating minerals, and the gains and losses of 'mobile' components are listed in Table 7. The numbers of the stoichiometric coefficients of the reactant phases were chosen based on a 100 cm³ product.
volume for the corona. Both samples J7205 and J0105 are taken as examples to model the fluxes and volume ratios during corona reactions. The calculated reactions (3)-(7) take into account the natural stoichiometry of the mineral phases (Tables 2-4) of interest, neglecting TiO₂, Cr₂O₃, ZnO and MnO; Fe₂O₃ was converted to FeO.

Reaction (3) can be written for the water absent corona assemblage (orthopyroxene+clinopyroxene+spinel) in sample J7205, in order to evaluate the modal proportions of the two reactants plagioclase and olivine,

\[ 0.583\text{Pl} + 1.148\text{Ol} + 0.123\text{Fe}^{2+} + 0.005\text{Ca}^{2+} = 0.592\text{Opx} + 0.592\text{Cpx} + 0.551\text{Spl} + 0.070\text{Mg}^{2+}. \] (3)

The molar amounts of ‘mobile’ components (Ca²⁺, Mg²⁺, Fe²⁺) are very small and may be the result of slight chemical variations in the analysed phases. Additionally, these small amounts are comparable with the uncertainty in estimating them. The approximate volumes of the corona minerals in reaction (3) are: plagioclase 59 cm³, olivine 51 cm³, orthopyroxene 38 cm³, clinopyroxene 40 cm³ and spinel 22 cm³ (Table 7). Following the mineral volumes of reaction (3), the clinopyroxene–spinel symplectite consists of 35% spinel and 65% clinopyroxene, which is similar to the proportions estimated by image analysis in the selected microdomains (Figs 2c,d & 7a). After reaction (3) a product volume of 100 cm³ corona is formed at the expense of 110 cm³ reactant phases, thus \( \Delta V = 10 \text{ cm}^3 \) (\( \Delta V = \text{Vol(products)} - \text{Vol(reactants)} \)). Reaction (3) is a solid–solid reaction hence the equilibrium conditions of this reaction are independent of any fluid phase potentially present in the rock. Thus, this reaction provides a useful geological thermometer and barometer. However, the absence of volatiles in reaction (3) does not imply fluid absent conditions during corona-forming reactions. Water was clearly necessary for the growth of amphibole in the corona. Mineral reaction textures suggest a partial consumption of orthopyroxene, spinel and plagioclase and in most of the observed cases a complete consumption of clinopyroxene during the formation of amphibole. Amphibole and clinopyroxene do not show intergrowth textures and/or equilibrium phase boundaries that would suggest a simultaneous growth of both minerals. Mineral reaction textures indicate that clinopyroxene and amphibole are not compatible in the reaction corona of sample J7205, and the latter formed at the
0.166Na_{0.01}Ca_{0.98}Mg_{0.02}Al_{2.00}Si_{1.99}O_{8}Pl + 0.371Mg_{1.53}Fe_{0.47}Ca_{0.01}Al_{0.08}Si_{1.95}O_{8}Opx
+ 0.207Mg_{0.46}Fe_{0.04}Al_{1.94}O_{8}Sp + 0.694Na_{0.01}Ca_{0.98}Mg_{0.49}Fe_{0.14}Al_{0.90}Si_{1.95}O_{8}Cpx
+ 0.343H_{2}O + 0.015Mg^{2+} + 0.183Na^{+} + 0.025K^{+} + 0.061F^{-}
= 0.370K_{0.07}Na_{0.51}Ca_{1.98}Mg_{5.51}Fe_{1.00}Al_{2.23}Si_{6.46}O_{23}
(F_{0.16}O_{1.86})Am + 0.012Fe^{2+} + 0.113Ca^{2+}. (4)

The calculated volume proportions of reaction (4) are in good agreement with textural observations where clinopyroxene is consumed by amphibole. As listed in Table 7, the volumes of reactant phases in reaction (4) are spinel 8 cm$^3$ < plagioclase 17 cm$^3$ < orthopyroxene 24 cm$^3$ < clinopyroxene 47 cm$^3$, to form a volume of 100 cm$^3$ amphibole.

The replacement of clinopyroxene by amphibole seems to be consistent with the shortening and coarsening of former fine-grained spinel rods embedded in the clinopyroxene layer compared to the amphibole + spinel symplectite (Figs 2c & 7a). This indicates spinel recrystallization and surface energy reduction during replacement of clinopyroxene by amphibole, similar to the metamorphic annealing of myrmekites (cf.
Ashworth, 1986b). The amphibole–orthopyroxene layer boundary is cusped towards the centre of the corona, in some parts orthopyroxene is missing (Fig. 2c,d) and amphibole is the only layer present suggesting that orthopyroxene is replaced by amphibole and leaves the inclusion-free amphibole layer behind. Single orthopyroxene inclusions within the amphibole layer (Fig. 6a,b) are relics of the incomplete replacement of orthopyroxene by amphibole.

The coronitic assemblage in sample J0105 and RSJ3105 separating olivine and plagioclase comprises orthopyroxene/amphibole/amphibole + spinel symplectite (Figs 2e,f, 3 & 6a). The former presence of clinopyroxene is uncertain, so the reactions are modelled without considering clinopyroxene as a reactant phase. For phase compositions approximate to those of sample J0105, the corona-forming reaction (5) could be,

\[
\begin{align*}
0.542\text{Na}_{0.02}\text{Ca}_{0.94}\text{Al}_{1.98}\text{Si}_{2.03}\text{O}_{6}\text{Pl} &+ 1.233\text{Mg}_{1.60}\text{Fe}_{0.30}\text{Si}_{1.00}\text{O}_{4}\text{Ol} \\
+ 0.256\text{H}_{2}\text{O} &+ 0.113\text{Na}^+ + 0.017\text{K}^+ + 0.013\text{F}^- \\
= 0.330\text{Mg}_{1.58}\text{Fe}_{0.37}\text{Ca}_{0.012}\text{Al}_{1.009}\text{Si}_{1.96}\text{O}_{6}\text{Opx} &+ 0.205\text{Mg}_{0.53}\text{Fe}_{0.87}\text{Si}_{1.00}\text{O}_{4}\text{Spl} \\
+ 0.262\text{K}_{0.06}\text{Na}_{0.47}\text{Ca}_{1.89}\text{Mg}_{5.42}\text{Fe}_{0.87}\text{Al}_{2.43}\text{Si}_{6.44}\text{O}_{23} &+ 0.004\text{Oh}_{1.05}\text{Am} + 0.033\text{Fe}^{2+} + 0.465\text{Mg}^{2+} \\
+ 0.010\text{Ca}^{2+}. &
\end{align*}
\]

(5)

The approximate volume proportions of reaction (5) are: olivine 55 cm³, plagioclase 55 cm³, orthopyroxene 21 cm³, spinel 8 cm³ and amphibole 71 cm³ and the volume decrease of reaction (5) is ~10 cm³. The residuals of reaction (5) require transport of Na and K, as well as F and H₂O into the corona, while Fe, Mg and Ca are removed (Table 7). A coeval growth of orthopyroxene and amphibole + spinel symplectite, as in reaction (5), was reported by Mongkolpit & Ashworth (1983) and Lang et al. (2004).

Magmatic v. metamorphic origin of newly formed orthopyroxene and amphibole

Mineral textures in samples J0105 and RSJ3105 show an incomplete replacement of orthopyroxene by amphibole suggesting, that orthopyroxene had formed before amphibole. Thus, these two minerals were never in equilibrium in samples J0105 and RSJ3105. The inner phase boundary of orthopyroxene, towards olivine is slightly undulating and the outer boundary towards amphibole is strongly irregular. Laths of orthopyroxene protrude into the amphibole layer (Fig. 2f) and also appear as isolated single inclusions within the amphibole layer (Fig. 6a). Despite ubiquitous corona orthopyroxene in samples J0105 and RSJ3105, its origin is equivocal. We stress that a magmatic origin for the orthopyroxene and at least some parts of the amphibole is possible. Both minerals
have recrystallized during high-\(T\) solid-state replacement (in the sense of replacing pre-existing minerals, without the presence of any melt) in the course of cooling at the gabbro–granulite transition.

In Fig. 3, coarse-grained olivine is in the centre part of the corona surrounded by an orthopyroxene layer of variable thickness ranging from few \(\mu\)m up to 300 \(\mu\)m. The narrow part of the orthopyroxene layer is adjacent to brownish Am I which is enriched in trace elements and REEs, relative to Am II and the wider part of the orthopyroxene layer (400 \(\mu\)m) is adjacent to Am II. The phase boundary between orthopyroxene and Am I as well as Am II is undulating, with amphibole cusps towards orthopyroxene implying a partial consumption of orthopyroxene by amphibole. It is suggested that cumulus olivine crystals become rimmed by a peritectic orthopyroxene layer before the orthopyroxene was replaced by an intercumulus magmatic amphibole phase Am I, enriched in Ti, V and REEs. Thus reaction (5) has to be modified to reaction (6),

\[
\begin{align*}
\text{0.442Na}_{0.02}\text{Ca}_{0.94}\text{Al}_{1.98}\text{Si}_{2.03}\text{O}_8\text{Pl} + 0.78\text{Mg}_{1.56}\text{Fe}_{0.37}\text{Ca}_{0.012}\text{Al}_{0.93}\text{Si}_{1.96}\text{O}_8\text{Opx} &+ 0.362\text{H}_2\text{O} + 0.035\text{Fe}^{2+} + 0.042\text{Mg}^{2+} + 0.295\text{Ca}^{2+} + 0.166\text{Na}^+ + 0.024\text{K}^+ + 0.018\text{F}^- \\
= 0.370K_{0.06}\text{Na}_{0.47}\text{Ca}_{1.89}\text{Mg}_{3.42}\text{Fe}_{0.87}\text{Al}_{2.45}\text{Si}_{6.44} &\text{O}_{23}(\text{F}_{0.05}, \text{OH}_{1.95})\text{Am.} \\
\end{align*}
\]

As the trace element and REE concentrations in olivine, orthopyroxene and plagioclase are strongly depleted relative to amphibole, the residuals in reaction (6) and also the increased concentrations in trace elements and REEs in Am I (Fig. 4a–d) may be provided by a stationary liquid phase trapped between orthopyroxene and plagioclase.

Reaction (7) can be written for the metamorphic formation of the spinel-bearing and inclusion-free amphibole layer, as long as a coeval formation of both layers is assumed,
that both phases are entirely used to form an amphibole + spinel symplectite. A certain amount of amphibole, produced in reaction (7), also forms the inclusion-free amphibole layer, between the symplectite and the orthopyroxene layer. Reaction (7) forms 10.3 cm$^3$ spinel and 89.7 cm$^3$ amphibole at the expense of 65.2 cm$^3$ plagioclase and 27.1 cm$^3$ orthopyroxene (Table 7). According to the image analyses of the amphibole + spinel symplectite the volume proportions of amphibole:spinel = 5:1, within the symplectite (Fig. 2e,f). Hence, 51.5 cm$^3$ amphibole and 10.3 cm$^3$ spinel form the symplectite layer, leaving behind a
38.2 cm³ inclusion-free amphibole layer. Reaction (7) is analogous to reaction (2) and involves a volume increase of 7.7 cm³ (+8.4%) and a gain of Fe, Mg, Ca, Na, K, F and H₂O.

Although, the stoichiometry of reactions (6) and (7) was modelled for mineral compositions of sample J0105, the amphibole/amphibole+spinel layers in sample RSJ3105 (Fig. 6a) are most likely the product of a similar reaction. In either case can the coronas be modelled as a ‘closed’ system (cf. Markl et al., 1998) except for H₂O, but in all cases the gains and losses of elements is very small and the main uncertainties for Mg and Fe may arise from the zoning in amphibole, even though only slight chemical variations are documented (Table 4).

Formation of orthopyroxene–magnetite symplectites

To a first approximation, the orthopyroxene–magnetite symplectite (Figs 2b–e & 7a) can be modelled by the simple reaction between fayalite (fa), forsterite (fo), quartz (qtz), magnetite (mag) and oxygen. For the replacement of olivine by magnetite and quartz, this reaction can be written according to the quartz–fayalite–magnetite oxygen buffer, whereby the fayalite component of olivine reacts with oxygen to form quartz and magnetite,

\[ 3\text{Fe}_2\text{SiO}_4 + 2\text{O} = 3\text{SiO}_2 + 2\text{Fe}_3\text{O}_4. \]  

(8)

Excess quartz from reaction (8) reacts with the remaining forsterite component of the olivine to form enstatite by reaction (9).

\[ \text{Mg}_2\text{SiO}_4 + \text{SiO}_2 = \text{Mg}_2\text{Si}_2\text{O}_6. \]  

(9)

Combining the two reactions (8) and (9) gives the orthopyroxene–magnetite formation after reaction (10) (Fig. 7b),

\[ 6(\text{MgFe})_2\text{SiO}_4 + 2\text{O} = 3\text{Mg}_2\text{Si}_2\text{O}_6 + 2\text{Fe}_3\text{O}_4. \]  

(10)

P–T relations of the corona reactions

Progress towards understanding the formation of reaction coronas between olivine and plagioclase can be made by constructing P–T diagrams using the simplified model system NCFMASH (Na₂O, CaO, FeO, MgO, Al₂O₃, SiO₂, H₂O) as shown in Fig. 8a–e, ignoring K and minor components. P–T pseudosections (Fig. 8a) and P–T Schreinemakers diagrams (Fig. 8e) were computed, using the free energy minimization program PERPLEX (Connolly, 1990 updated October 2009) and the updated thermodynamic data set (file hp04ver.dat) of Holland & Powell (1998). The solid-solution models used were: Amph(DHP) (amphibole, Dale et al., 2000), Cpx(HP) (clinopyroxene, Holland & Powell, 1998), feldspar (plagioclase, Fuhrman & Lindsley, 1988), melt(HP) (melt, White et al., 2001), O(HP) (olivine, Holland & Powell, 1998), Opx(HP) (orthopyroxene, Powell & Holland, 1999), and Sp(HP) (spinel, Holland & Powell, 1998). The effective corona bulk for the sample J7205 was calculated based on the stoichiometric coefficients of the metamorphic product minerals in reaction (3), which
Fig. 8. (a) A $P-T$ pseudosection constructed in NCFMASH system for the calculated layer bulk chemistry (in wt%): Na$_2$O = 0.03, MgO = 16.68, Al$_2$O$_3$ = 29.44, SiO$_2$ = 33.98, CaO = 7.98, FeO = 11.39, H$_2$O = 0.5. The $P-T$ path starts at $>900^\circ$C in the Pl–Ol–Spl–Opx–H$_2$O field and crosses the Pl–Ol–Spl–Opx–Cpx–H$_2$O field into the Pl–Spl–Opx–Cpx–H$_2$O field. The anticlockwise metamorphic path is derived by comparing the observed mineral assemblage in the thin section with the computed model assemblage and the mineral mol.% isopleths in (b), (c) & (d). The relevant reactions (3) and (4) are indicated. (e) A section of a Schreinemakers diagram in the simplified iron-free end-member system CMASH for the relevant corona-forming reactions (3) and (4). Activity corrected phases according to their natural composition are used. The invariant point lies at 750 °C and 5.2 kbar.
are clinopyroxene = 0.592, orthopyroxene = 0.592 and spinel = 0.551. This results in an effective layer bulk composition (in wt%) of Na2O = 0.03, MgO = 16.68, Al2O3 = 29.44, SiO2 = 33.98, CaO = 7.98, FeO = 11.39 and H2O was assumed to be 0.5 wt%. Mineral mol.% isopleths of the respective minerals are shown in Fig. 8b–d.

A P–T Schreinemakers diagram was computed for the representative model reactions (3) and (4) in the simplified chemical system CMASH (CaO, MgO, Al2O3, SiO2, H2O, neglecting Na2O) involving the activity corrected end-members: anorthite (a_an = 0.99), forsterite (afo = 0.61), spinel (a_sp = 0.53), enstatite (a_en = 0.58), diopside (a_di = 0.77), tschermakite (a_ts = 0.08) (activity correction was done to take account for non-CMASH components). End-member mineral activities were calculated based on the mineral compositions of sample J7205 using the mixing models of the program AX (Holland & Powell, 1998), except tschermakite (a_ts = 0.08). The mineral chemistry of amphibole suggests a tschermakite activity < 0.08. However a lower tschermakite activity would stabilize tschermakite to unreasonably high temperatures, thus an a_an of 0.08 was chosen to get the best fit between the tschermakite stability in both the P–T pseudosection (Fig. 7a) and the P–T section Schreinemakers diagram (Fig. 7e), respectively. The fixed mineral activities are an approximation and may not reflect the true mineral compositions at the time of corona formation because of possible compositional reequilibration during cooling.

According to the phase-field stability of olivine+plagioclase in Fig. 8a, and a calculated liquidus temperature of 1358 °C (Table 1), the P–T trajectory starts in the Pl-OI-Spl-Opx–H2O field at >900 °C and <6 kbar. Growth of the anhydrous corona assemblage orthopyroxene+clinopyroxene + spinel (Fig. 2c,d) at the expense of olivine and plagioclase is indicated by the mineral mol.% isopleths in Fig. 8b–d and constrains an increase in pressure during cooling. The P–T trajectory crosses the estimated peak P–T conditions of the surrounding magmatites at 850 to 800 °C and 6–7 kbar (Otamendi et al., 2008; Gallien et al., 2009, 2010). The replacement of corona clinopyroxene and orthopyroxene by amphibole in the course of isobaric cooling is the latest event and led to the formation of an inner inclusion-free amphibole layer and an outer amphibole + spinel symplectite layer.

**Phase equilibrium constraints on chemical potentials for reaction coronas**

The multi-layer coronas may involve the simultaneous growth of each layer at constant P–T or develop via a multistage evolution at changing P–T conditions. The thermodynamic incompatibility of the reactant minerals at the gabbro–granulite transition and the phase equilibria of the coronitic assemblage during subsequent cooling were modelled using calculated chemical potentials of μMgO–μCaO as axes on phase diagrams. Based on the assumption that the corona minerals are stable along a gradient in the chemical potentials (μ), the phase relations of olivine, plagioclase and their reaction products are shown in the simplified μMgO–μCaO grid (Fig. 9c–g). Thus MgO and CaO are the mobile components, allowing component transport within the reaction rim, and Al2O3, SiO2, H2O are treated as unconstrained components.

The calculations in Fig. 9c–g were done by using the activity corrected end-members of forsterite, enstatite, diopside, tschermakite, spinel and anorthite according to their natural compositions (Tables 2–4). The anhydrous corona assemblage orthopyroxene+clinopyroxene + spinel between olivine and plagioclase indicates that the rates of metamorphic reactions were controlled by diffusion of dissolved species along a reaction zone (cf. Fisher, 1977; Mongkolpit & Ashworth, 1983; Johnson & Carlson, 1990; Lang et al., 2004). It is assumed that the number of layers and the succession of the mineral layers within the corona are mainly governed by chemical potential gradients and by different diffusivities of the various components (Fisher, 1977). The chemical potential gradients between olivine and plagioclase yield to an outward diffusion of Mg (Fe) from olivine into the corona while Ca and Al diffuse in the opposite direction from matrix plagio-

Fig. 9. (a) Schematic illustration of the textural relations of olivine and plagioclase separated by the reaction corona comprising an inner layer of orthopyroxene and an outer layer of clinopyroxene/amphibole + spinel. The arrow heads indicate the net transfer of MgO, FeO, CaO and Al2O3 from olivine and plagioclase into the corona. The suggested original olivine–plagioclase phase boundary is shown. The possible end-member reaction is given. (b) Schematic illustration of the reaction layer. (c)–(g) The phase relations of the coronitic assemblage are shown in the μMgO–μCaO space (unconstrained amounts are: SiO2, Al2O3 and H2O) at variable temperatures and a constant pressure of 6.5 kbar. (c) The olivine–plagioclase stability field in the μMgO–μCaO space is shown. The white arrows indicate the decreasing stability of olivine and plagioclase during cooling. (d) The thermodynamic instability of anorthite and olivine at < 840 °C led to the formation of an orthopyroxene+clinopyroxene + spinel reaction layer. (e) At 830 °C an inner orthopyroxene layer and an outer clinopyroxene + spinel layer are formed. The white arrows indicate the direction of layer growth, suggesting that orthopyroxene grows at the expense of olivine and clinopyroxene + spinel migrate outward into plagioclase. (f) At < 770 °C amphibole is stable at the low μMgO side. The inset shows an enlargement of the area in the box. (g) Processes of amphibole formation are shown. Clinopyroxene + spinel become replaced by amphibole [phase-field transition (2)–(3)]; inclusion-free amphibole replaces orthopyroxene [phase-field transition (4)–(1)]; an amphibole + spinel symplectite migrates outward at the expense of plagioclase (phase-field transition (5) – anorthite).
THE ORIGIN OF MULTI-LAYER CORONAS

(a) $2 \text{Fo} + \text{An} = 2 \text{En} + \text{Di} + \text{Spl}$

(b) Forsterite (Fo) + Anorthite (An) + original Fo-An interface

(c) Decreasing An + Fo stability at lower $T$

(d) Incipient corona formation at $T < 836 \degree C$

(e) Anorthite + forsterite are not stable

(f) Amphibole replaces orthopyroxene and clinopyroxene

(g) Orig. Fo-An interface of anhydrous coronas

Endmember activities:
- $\text{An} = 0.98$
- $\text{Di} = 0.70$
- $\text{En} = 0.57$
- $\text{Fo} = 0.59$
- $\text{Sp} = 0.61$

Endmember activities:
- $\text{An} = 0.99$
- $\text{Di} = 0.77$
- $\text{En} = 0.58$
- $\text{Fo} = 0.61$
- $\text{Sp} = 0.53$
- $\text{Ts} = 0.08$

Forsterite Anorthite

Original Fo-An interface

Anhydrous coronas are formed

Amphibole replaces orthopyroxene and clinopyroxene
clase. Further, it is assumed here that the system is closed to diffusion (except for H$_2$O and neglecting the loss and gains in components, as described above) beyond the layer contacts with olivine and plagioclase and also that the growth of the multi-layer corona happens due to solid-state replacement of pre-existing phases. The original situation for the olivine–plagioclase equilibrium is shown in Fig. 9a,b. The stability field of olivine–plagioclase covers a wide range in $\mu$MgO–$\mu$CaO space at $>850 \, ^\circ$C (Fig. 9c) and is stable down to $836 \, ^\circ$C. During initial cooling, the plagioclase–olivine stability field progressively shrinks (Fig. 9d), until corona-forming reactions commence at $<836 \, ^\circ$C. Below this temperature, olivine and plagioclase (red field in Fig. 9e) are no longer stable and consequently become separated by the corona-forming minerals orthopyroxene, clinopyroxene and spinel, and at lower temperatures by tschermakite. The $\mu$MgO of the olivine-bearing phase field is higher than the corresponding $\mu$MgO of the plagioclase stability fields. This indicates the thermodynamic incompatibility of olivine and plagioclase under granulate facies temperatures at medium pressure (6.5 kbar). Furthermore it can be shown, that the minerals of the ‘water-free’ multi-layer corona grow simultaneously at constant $P$–$T$ (Fig. 9e).

In sample J7205, plagioclase and olivine, once in equilibrium, get consumed due to solid-state replacement at $<840 \, ^\circ$C by a reaction corona, comprising orthopyroxene|clinopyroxene+spinel. Petrographic observations in sample J7205 (Fig. 2b,c) corroborate the modelled reaction corona in $\mu$MgO–$\mu$CaO space (Fig. 9e), where the phase fields (1) and (2) represent the inner shell composed of orthopyroxene and the outer clinopyroxene+spinel layer, respectively. The growth direction of each individual layer is indicated by the arrow heads in Fig. 9e, suggesting a migration of the orthopyroxene layer inward (at the expense of olivine), while the clinopyroxene+spinel layer simultaneously migrates outward into plagioclase. In that case, the original olivine–plagioclase interface would be directly at the orthopyroxene|clinopyroxene+spinel layer contact. Continuing isobaric cooling (<774 °C, Fig. 9f) increases the stability of amphibole and decreases the stability of clinopyroxene and orthopyroxene. The required H$_2$O for the amphibole formation likely diffused along grain boundaries (Dowty, 1980). The first stability of amphibole appears on the low $\mu$MgO side, at the clinopyroxene and orthopyroxene–plagioclase phase boundary at 774 °C. As amphibole is stable, there are two main reaction fronts migrating through the corona. An outer reaction front replaces clinopyroxene and leaves the coarse-grained amphibole+spinel symplectite behind [Fig. 9g, phase-field transition (2)–(3)] and an inner reaction front migrates into orthopyroxene to form the inclusion-free amphibole layer [Fig. 9g, phase-field transition (1)–(4)] (for mineral microstructure see Fig. 2b,c). The migration direction of the amphibole layer as well as the order of the layer sequence within the model corona of sample J7205 are well demonstrated by the phase relations in the $\mu$MgO–$\mu$CaO space and corresponds to the petrographic observations (Fig. 2b,c).

In the clinopyroxene absent coronas (samples J0105 and RSJ3105) amphibole occurs as large annealed single crystals (Fig. 6a,b). It is suggested, that the inclusion-free and the spinel-hosting amphibole layers are the products of different precursor minerals. Similar to sample J7205, it is also suggested, that the inclusion-free amphibole in samples J0105 and RSJ3105 grew at the expense of orthopyroxene. Isolated orthopyroxene inclusions within the inclusion-free amphibole layer (Fig. 6a) and thin, elongated orthopyroxene sticking out into the inclusion-free amphibole layer (Fig. 2e) are consistent with the replacement of orthopyroxene through an inward migrating amphibole layer along the phase-field transition (1)–(4) in Fig. 9g. It is suggested that in samples J0105 and RSJ3105, plagioclase (not clinopyroxene) is replaced by an outward migrating amphibole–spinel symplectite [see arrow heads at the transition between the phase field (5) and anorthite in Fig. 9g], to form the outer shell of the corona in J0105 and RSJ3105.

**Diffusion and symplectite formation**

Chemical potential gradients and different diffusivities of Mg, Al, Ca and Si (neglecting Fe and minor components) between adjacent olivine and plagioclase led to the multi-layer sequence comprising orthopyroxene|amphibole|clinopyroxene+spinel (amphibole + spinel) at granulate facies conditions. Mg diffuses outward from the olivine–orthopyroxene boundary across the whole reaction corona while Al and Ca were less mobile. Consequently the layers hosting spinel formed by consumption of plagioclase (= outward migration of the amphibole/spinel layer), driven by ‘fast’ outward diffusion of Mg. Ca and Al diffusion into the opposite direction led to the inward migration of the pure amphibole layer at the expense of orthopyroxene. In general the amphibole layer hosting spinel is thicker than the inclusion-free amphibole layer (Figs 2e,f, 3a & 5a), indicating higher mobility of Mg than Al and Ca. The outward diffusion of Mg (and Fe) across the whole reaction band corroborates the assumption that neither MgO nor FeO are the rate limiting components that are responsible for corona formation. Similar component mobilities were reported by Abart et al. (2001). They suggested a slower diffusivity of Ca than Al in scenarios with high Mg diffusivity, such as the case at the olivine–plagioclase interface in this study. The occurrence of amphibole + spinel and clinopyroxene + spinel symplectite in the coronas indicates the relative immobility of Al and Si in geological systems (Griffith & Heier, 1973; Ashworth & Sheplev, 1997; Lang & Gilotti, 2001). The formation of spinel-bearing symplectite implies re-
stricted diffusion of at least two components. If only one component had a restricted diffusion range, then the faster diffusion rates of the others would compensate this relative immobility to form only one large volume of a single mineral (Griffin, 1971; Mongkoltip & Ashworth, 1983).

**Annealing and conservation of the layer sequence**

Before annealing, polycrystalline laths of minerals perpendicular to the layer contact comprised the corona. Chemical mass transfer thus could occur by a combination of volume and grain boundary diffusion across the layered sequence, as volume diffusion is several orders of magnitude slower than grain boundary diffusion (Joesten, 1991; Lasaga, 1998). Grain boundary diffusion is considered to be the main contributor to mass transport at incipient corona formation (cf. Keller et al., 2006, 2008). The high-\( T \) annealing of former polycrystalline orthopyroxene and amphibole laths oriented perpendicular to the layer contact led to optically continuous orthopyroxene and amphibole layers, respectively (Fig. 6b). After annealing of the polycrystalline mineral layers to optically continuous ‘single’ mineral layers (Fig. 6b), the loss of grain boundaries within each layer limited the possibility of grain boundary diffusion across the layers and the slower processes of volume diffusion became more important. The slower volume diffusion process prevents completion of the corona-forming reactions, in the sense of a total consumption of the reactant minerals. Consequently the annealing process may have ‘sealed’ parts of the corona to maintain the internal structure even though chemical potential gradients still exist across the layered structure. Thus, such structures reflect the inefficient diffusion of one or more elements within a certain volume of the reaction corona (cf. White et al., 2008).

**SUMMARY AND CONCLUSIONS**

**P–T evolution**

The three investigated samples, J7205, J0105 and RSJ3105 record recrystallization of a magmatic mineral assemblage, mainly comprising olivine, plagioclase, clinopyroxene and orthopyroxene, at granulite facies conditions. An anticlockwise metamorphic P–T path with final isobaric cooling from temperatures above 850 \( \text{°C} \) at 6–7 kbar is inferred from mineral reaction textures and computed P–T pseudosections and P–T Schreinemakers diagrams. In all samples, olivine and plagioclase are separated by a continuous multi-layer corona comprising (i) olivine|orthopyroxene|clinopyroxene + spinel|plagioclase (sample J7205) or (ii) ±olivine|orthopyroxene|amphibole|amphibole+ spinel|plagioclase (sample J0105 and RSJ3105). Based on mineral textures and trace element and REE characteristics two different corona types are documented and their mechanisms of formation are summarized here.

**Corona-forming processes**

The multi-layer coronas between olivine and plagioclase in gabbroic rocks from Valle Fértel and La Huerta Ranges are interpreted as reaction zones that formed at the original interface between two mutually incompatible minerals during cooling at the gabbro–granulite transition. The chemical potential gradients and differences in the diffusivity of MgO and CaO are the driving force for the corona formation (cf. Fisher,

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**Fig. 10.** The sketch illustrates the formation history of the multi-layer corona in sample J0105. (a) In the first stage a peritectic orthopyroxene layer of constant width evolves from a liquid between cumulate olivine and plagioclase. (b) Interstitial, brownish Am I, enriched in trace elements and REEs evolves from a late magmatic stationary melt phase trapped in convex embayments in the intercumulus space. At this stage, olivine is already rimmed by orthopyroxene. Thus, Am I may have consumed parts of the orthopyroxene layer, which results in a thinning of the orthopyroxene layer width. (c) Pale green Am II + spinel symplectite depleted in trace elements and REEs, relative to Am I forms on the expense of orthopyroxene and plagioclase during cooling. The inclusion-free Am II migrates inward, at the expense of orthopyroxene and the amphibole + spinel symplectite migrates outward into plagioclase.
This involves a net transfer of Mg and Fe from olivine into the corona and of Ca and Al from plagioclase.

Finally the evolution of the described coronitic assemblage can be summarized as follows:

1. Metamorphic solid-state replacement of pre-existing olivine and plagioclase led to the anhydrous multi-layer sequence of orthopyroxene–clinopyroxene + spinel symplectite in sample J7205.

2. During cooling, metamorphic amphibole forms at the expense of fine-grained clinopyroxene + spinel (in sample J7205) and orthopyroxene leaving a coarse-grained amphibole + spinel symplectite and an inclusion-free amphibole layer behind. The coarse-grained spinel rods in amphibole indicate surface energy reduction during replacement of the clinopyroxene + spinel symplectite by amphibole.

3. In J0105 intercumulus olivine reacted with a stationary, interstitial liquid to form peritectic orthopyroxene (Fig. 10a). Brownish Am I enriched in trace elements and REEs evolved from an interstitial residual melt, trapped between plagioclase and peritectic orthopyroxene in sample J0105 (Fig. 10b).

4. Mineral reaction textures between orthopyroxene, Am II and plagioclase in samples J0105 and RSJ3105 indicate a partial metamorphic solid-state replacement of orthopyroxene by an inward migrating inclusion-free Am II layer. The amphibole + spinel symplectite layer migrates in the opposite direction and consumes plagioclase (Fig. 10c). Thus amphibole and orthopyroxene were never in equilibrium and a coeval formation of both minerals due to metamorphic solid-state replacement of pre-existing mineral phases did not happen.

5. The oxidation of the fayalite component in olivine led to the formation of orthopyroxene–magnetite symplectites.

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