Na-Al-rich gedrite coexisting with hornblende in a corona between plagioclase and olivine

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Abstract

In an olivine dolerite in the Arttjålet gabbro (Sweden) metamorphism has resulted in the formation of double-shell coronas between olivine and plagioclase. One shell consists of orthopyroxene, the other contains coexisting gedrite and hornblende. The gedrite,

\[ \text{Na}_{0.88}(\text{Na}_{0.08}\text{Ca}_{0.09}\text{Mn}_{0.07}\text{Fe}^{2+}_{1.76})(\text{Fe}^{2+}_{1.26}\text{Mg}_{2.33}\text{Fe}^{3+}_{0.10}\text{Al}_{1.28})(\text{Al}_{2.19}\text{Si}_{5.81})\text{O}_{22}(\text{OH})_{2} \]

is the most Na- and Al-rich orthoamphibole yet found coexisting with hornblende. The hornblende has the composition

\[ \text{K}_{0.07}\text{Na}_{0.76}(\text{Na}_{0.20}\text{Ca}_{1.52}\text{Mn}_{0.03}\text{Fe}^{2+}_{22})(\text{Fe}^{2+}_{1.78}\text{Mg}_{1.82}\text{Fe}^{3+}_{0.22}\text{Ti}_{0.01}\text{Al}_{1.17})(\text{Al}_{2.04}\text{Si}_{5.96})\text{O}_{22}(\text{OH})_{2} \]

The corona is inferred to have formed at \( T = 500-550^\circ\text{C}, P > 5 \text{ kbar}, \) a relatively low water fugacity, and oxygen fugacity near the eFM buffer. It is suggested that the high Al and Na contents of the gedrite are due to limited mobility of Si and Al during corona formation, in combination with a Na excess. The occurrence of gedrite in the corona is attributed mainly to the high Na/Ca ratio of the original plagioclase.

Introduction

In their comprehensive review of the metamorphic amphiboles Robinson et al. (1982) have illustrated the possibilities offered by amphibole compositions as guides to metamorphic conditions. A prerequisite for understanding the effects of intensive parameters on amphibole compositions is knowledge of the crystal-chemical control exerted by the amphibole itself (internal limits of Robinson et al.). Coexisting amphiboles provide information on such crystal-chemical limits, since their compositions outline a miscibility gap or a solvus.

The present paper relates the occurrence of aluminous orthoamphibole (gedrite) and hornblende in a corona between olivine and plagioclase. The origin of the amphiboles and the implications with regard to crystal chemistry are considered.

Geological setting

The host rock for the two amphiboles is an olivine dolerite (sample 158), one of a series of dolerites that occur in the Arttjålet gabbro (Central Swedish Caledonides). This gabbro intruded nearly simultaneously with the peak of a medium-pressure \( (P > 5 \text{ kbar}) \), lower amphibolite-facies metamorphism of the country rocks (Senior and Otten, in press). The dolerites intruded the gabbro, while it was still hot, shortly after solidification (Otten, 1983). At a later stage, concurrent with regional retrogression under epidote-amphibolite-facies conditions, both gabbro and dolerites were metamorphosed to a variable extent. This metamorphism was the result of the introduction of water along cracks that were formed during a regional deformation phase. The degree of metamorphism in the gabbro and dolerites varies from incipient reaction rims between magmatic minerals to complete alteration over distances of a few centimeters from the cracks (Otten, 1983).

Petrography

The original olivine dolerite was subophitic and consisted of ca. 40% modal plagioclase, 40% augite, 5 to 10% ilmenite and subordinate brown hornblende and olivine. Plagioclase (An47) forms subhedral to anhedral tabular grains up to 3 mm in length. Augite (Ca41Mg35Fe24) occurs as finer anhedral grains in aggregates interstitial to plagioclase. Ilmenite (Hm < 5) forms amoeboid to graphic (skeletal?) grains up to several mm in length. Brown hornblende (up to 3.9 wt% TiO2, usually strongly altered, see below) occurs as anhedral, strongly poikilitic grains up to 1 cm in size. The nature of olivine (probably Fo45, see below) is difficult to assess due to complete alteration.
to cummingtonite–magnetite symplectites. It appears to have been amoeboid, occurring interstitially to plagioclase.

Metamorphic orthopyroxene, blue-green hornblende, gedrite, cummingtonite, magnetite and a few small grains of biotite and spinel make up between 10 and 20% of the olivine dolerite. Orthopyroxene, blue-green hornblende and gedrite occur in double-shell coronas between plagioclase on one side and cummingtonite-magnetite symplectites on the other (Fig. 1). Orthopyroxene occupies the shell adjacent to the symplectites and the two amphiboles form the shell against plagioclase. The shells are palisade-like aggregates of elongated, anhedral grains. The amphibole shell is usually thicker (typical thickness between 0.1 and 0.2 mm) than the orthopyroxene shell (0.1 mm). The gedrite makes up less than ten percent of the amphibole shell. It is nearly impossible to optically distinguish the gedrite from the blue-green hornblende due to the very fine grain size, anhedral nature, similar though fainter pleochroism (gedrite very pale gray to pale grayish green, hornblende colorless to pale blue-green) and strong overlap between adjacent grains in the coronas. The gedrite is, however, readily detected in backscattered-electron images in the electron microprobe.

Blue-green hornblende is also found as rims around ilmenite, aegirite and brown hornblende. The rims around the ilmenite are palisade-like aggregates similar to the amphibole shell of the corona, but do not contain gedrite. The rims around aegirite and brown hornblende usually consist of single grains of blue-green hornblende that have a homovalent relationship with the aegirite and brown hornblende (cf. Otten, 1983). The latter two usually show strong internal alteration as well, containing abundant exsolved rutile and ilmenite particles (cf. Mongkolpit and Ashworth, 1983; Otten, 1983).

Cummingtonite forms small, equant, multiply twinned anhedral grains, that replace the orthopyroxene of the corona and occur in symplectites with magnetite (Fig. 1). The cummingtonite-magnetite symplectites are nearly opaque in transmitted light, but in reflected light it is clear that the cummingtonite predominates over the magnetite. The magnetite generally forms very thin (ca. 1 μm) vermicules. The distribution of magnetite vermicules that have similar shape and orientation often delineates domains in the symplectites (Fig. 1).

Double-shell coronas consisting of orthopyroxene in one shell and hornblende or hornblende-spinel symplectite, but no gedrite, in the other, are frequently found between plagioclase and olivine in the Artfjället gabbro and dolerites (Otten, 1983). In view of the similarity between these coronas and the gedrite-bearing coronas, it is likely that the latter also formed between plagioclase and olivine and, hence, that the cummingtonite-magnetite symplectites are alteration products of olivine. This is
consistent with the bulk composition of the symplectites, which is close to that of olivine with Fo₄₅. Because coronas develop only in the presence of olivine and magnetite is absent in the orthopyroxene shell of the corona, the formation of the symplectites is inferred to postdate the coronas.

Magnetite-bearing symplectites, but with orthopyroxene as host mineral, have been found as alteration products of olivine in a few samples from the Artjälet gabbro and dolerites (Otten, 1983). In these orthopyroxene-magnetite symplectites each domain of magnetite vermicules with similar orientation and shape represents a separate grain of host orthopyroxene. The domains in the cummingtonite-magnetite symplectites, however, do not correspond to separate cummingtonite grains and grain boundaries of the cummingtonite frequently transect magnetite domains. It is suggested, therefore, that these symplectites originated as orthopyroxene-magnetite intergrowths and that the orthopyroxene, together with part of the corona orthopyroxene, was subsequently replaced by cummingtonite.

The inferred sequence of metamorphic reactions in the dolerite is then: (1) formation of orthopyroxene, blue-green hornblende and gedrite in coronas between olivine and plagioclase and formation of blue-green hornblende rims around ilmenite, augite and brown hornblende; (2) formation of orthopyroxene-magnetite symplectites from the remaining olivine; (3) formation of cummingtonite from orthopyroxene in coronas and symplectites.

**Mineral chemistry**

Wave-length dispersive electron-microprobe analyses were performed on a Cambridge Instruments Ltd. Microscan 9 with dead-time, probe drift and ZAF corrections by an on-line PDP 11/05 computer. Operating conditions were: accelerating voltage 20 kV, probe current 25 nA and 25 sec counting time, except for F and Cl, where probe current was 250 nA and counting time 50 sec. However both F and Cl were below detection limit (F < 0.05, Cl < 0.01 wt%).

Analyses of corona orthopyroxene, blue-green hornblende, gedrite, and cummingtonite are presented in Table 1. The amphibole analyses are averages of five to ten separate analyses, the orthopyroxene analysis is an average of three. Except for slight variations in Fe and Mg and, to a lesser extent, Si and Al in hornblende and gedrite (cf. Table 1), mineral compositions are uniform throughout the sample. Variations in Fe, Mg, Si, and Al in hornblende and gedrite are correlated and the distribution coefficients for Al-Si (1.11±0.03) and Fe-Mg (1.10±0.02) between adjacent grains of gedrite and hornblende are constant.

Because it could not be analyzed directly, ferric iron was estimated. The orthopyroxene formula does not allow the presence of ferric iron since it is already slightly cation-deficient (probably due to slightly high SiO₂ in the analyses). The cummingtonite may contain only minor ferric iron or else sites other than the A-site are partly vacant. Following Robinson et al. (1982) ferric iron in the hornblende and gedrite has been estimated by finding a reasonable balance between Na and Fe + Mn occupancies of the M4 sites. For the hornblende a value of 0.2 Na on M4 is reasonable (J.C. Schumacher, pers. comm. 1982), resulting in 0.28 Fe + Mn on M4 and a ferric iron ratio (Fe⁢³⁺/Fe⁢⁰⁶) of 0.1. The latter ratio is consistent with formation near the QFM buffer (cf. Spear, 1981a). For the gedrite a value of 0.08 Na on M4, suggested by Robinson et al. (1982), is used, yielding a ferric iron ratio of 0.03.

Magnetite in the symplectite is nearly pure Fe₃O₄, containing less than 1.5 wt% other elements (Al, Ti, V and Mn).

**Conditions of formation**

Quantitative estimates of the conditions during metamorphism are not possible on the basis of the data for the
gedrite-bearing dolerite alone, but some inferences can be
made because the metamorphism in the dolerite is related
to that of the enveloping gabbro.

The temperature of metamorphism has been estimated
from the compositions of coexisting garnet and biotite
and of hornblende and plagioclase in metagabbro- and
metadolomite samples (Otten, 1983). Zoning in garnet
presented a complication, the core compositions yielding
440–485°C, and the rim 520–580°C, using the Ferry and
Spear (1978) calibration. The hornblende-plagioclase
thermometers of Spear (1980a, 1981b) gave temperatures
generally between 500 and 550°C. Even though the horn-
blende–plagioclase thermometers are not accurately cali-
brated, they indicate temperatures similar to those for the
garnet rims. It is suggested, therefore, that the tempera-
ture during metamorphism was roughly 500–550°C.

A lower limit for the total pressure is provided by the
breakdown of magmatic plagioclase to albite and zoisite
in the gabbro and dolerites (cf. Otten, 1983). Extrapola-
tion of the results of Goldsmith (1982) to lower pressures
suggests water pressures and, hence, minimum total
pressure in excess of 5–6 kbar for a temperature between
500 and 550°C.

For the water fugacity only a rough indication can be
given. The introduction of water into dry rock such as the
gabbro or dolerites probably results in strong gradients in
water fugacity away from the feeder channels (cracks).
The presence of such gradients is consistent with an
increase in the degree of metamorphism and with changes
in mineralogy towards the cracks. The sequence at which
metamorphic minerals appear on approaching a crack
usually is: orthopyroxene and blue-green hornblende
(coronas and pyroxene rims); cummingtonite (replaces
magnatic and corona orthopyroxene); albite and zoisite
(replace magmatic plagioclase) (cf. Otten, 1983). The
breakdown of magmatic plagioclase to zoisite and albite
requires high water fugacities (cf. Goldsmith, 1982). The
presence of orthopyroxene in coronas instead of cum-
mingtonite on the other hand probably reflects a relatively
low water fugacity. It is likely that the formation of
cummingtonite occurred at an intermediate water fugac-
ity in view of its position between orthopyroxene–horn-
blende and zoisite–albite. By analogy with the
metamorphism in the gabbro, the development of ortho-
pyroxene–hornblende–gedrite coronas in the gedrite-
bearing dolerite is thought to have occurred at relatively
low water fugacities, with the subsequent formation of
the cummingtonite reflecting an increase in water fugac-
ity.

The development of the orthopyroxene-magnetite sym-
plectites from olivine takes place through the oxidation
reaction

\[ 3 \text{Fe}_2\text{SiO}_4 + \frac{1}{2} \text{O}_2 = \text{Fe}_5\text{O}_4 + 3 \text{FeSiO}_3 \]

Because this oxidation reaction postdates the develop-
ment of the coronas, it provides an upper limit for the
oxygen fugacity during corona formation. The upper
stability limit for the olivine is estimated from the thermo-
dynamic data of Nitsan (1974), using a magnetite activity
of 1 and assuming \( \text{Fo}_{45} \) for the olivine and \( \text{En}_{54} \) for the
orthopyroxene. The latter equals the \( \text{Mg} / (\text{Mg} + \text{Fe}) \) ratio
in the cummingtonite by which the orthopyroxene was
replaced. The calculated boundary lies ca. 2 log units
above the QFM buffer curve (from Myers and Eugster,
1983). Formulations of activity coefficients different from
those employed by Nitsan (1974), e.g., those of Engi
(1980) and Sack (1980), yield a slightly lower oxygen
fugacity for the reaction boundary. Olivine-tholeiites
such as the gedrite-bearing dolerite (cf. Otten, 1983)
solidify at oxygen fugacities slightly below (ca. 1 log
unit) the QFM buffer (Morse, 1980) and follow a cooling
path parallel to this buffer (Haggerty, 1976). Hence,
during corona formation the oxygen fugacity must have
been between ca. 1 log unit below and at most 2 log units
above the QFM buffer.

**Corona origin**

In order to assess whether the gedrite and hornblende
in the corona formed in equilibrium and, hence, are truly
coexisting amphiboles, it is necessary to examine how
they formed. Coronas between olivine and plagioclase are
frequently found in olivine gabbro and troctolites (cf.
These coronas generally have one shell of orthopyroxene
and one consisting of a symplectitic intergrowth between
spinel and clinopyroxene or hornblende. The formation of
these coronas has been attributed to deuteric reaction
during cooling of the magmatic rocks (Griffin and Heier,
1973; Gardner and Robins, 1974) or to (retrograde) meta-
orphism (Whitney and McLelland, 1973; van Lamoen,
1979; Mongkolpit and Ashworth (ms., submitted to Jour-
nal of Petrology). Otten (1983) concluded that the coronas
in the Artfiiillet gabbro and dolerites are due to metamor-
phism, not a deuteric reaction. The orthopyroxene–horn-
blende–gedrite coronas under consideration here are a
variant of orthopyroxene–hornblende–spinel coronas
elsewhere in the Artfiiillet gabbro and dolerites. Discuss-
sion will be limited, therefore, to the origin of hydrous,
hornblende-bearing coronas.

Models for the olivine–plagioclase reaction have been
based on various assumptions (cf. Mongkolpit and Ash-
worth, ms.) such as closed-system (excluding \( \text{H}_2\text{O} \) addi-
tion) or open-system reaction and a migrating or a fixed
boundary between orthopyroxene and hornblende.
Mongkolpit and Ashworth (ms.) provide a quantitative
model for corona formation that is not based on such
initial assumptions. They show that the fine-scale sym-
plectitic intergrowth between hornblende and spinel, a
feature that was neglected by previous authors, is due to
limited mobility of Al and Si. Orthopyroxene formation is
not the result of Si addition, but of loss of Fe and Mg from
the olivine. Components other than Si and Al are more
mobile and during corona formation loss or gain of Mg,
Fe, Ca, Na etc. may occur.
The restricted mobility of Al and Si implies that the bulk composition of the hornblende shell, including the intergrown spinel, must have the same Al/Si ratio as the reactant plagioclase (Mongkoltip and Ashworth, ms.). This constancy of Al/Si is borne out by analytical data of van Lamoen (1979), Nishiyama (1983), Otten (1983) and Mongkoltip and Ashworth (ms.). The assertion of Nishiyama (1983) that the Na/Ca ratio remains constant during corona formation is contradicted by his own analytical data, which indicate open-system behavior with regard to these elements.

The same restricted mobility of Al and Si, deduced from the spinel-bearing coronas, is thought to apply to the gedrite-bearing corona on the basis of the similarity of Al/Si ratios in plagioclase (0.58), blue-green hornblende (0.52–0.56) and gedrite (0.58–0.62). Unlike spinel and hornblende in spinel-bearing coronas, the gedrite and hornblende are not constrained to form symplectites, because their Al/Si ratios are similar and their location is independent, therefore, of the mobility of Al and Si.

Because corona formation is a kinetic process, one may not assume that the corona minerals represent an equilibrium assemblage (Mongkoltip and Ashworth, ms.). The immobility of Al and Si suggests the presence of concentration gradients for these elements across the corona from the olivine to the plagioclase. It is unlikely, therefore, that the orthopyroxene in the one shell and the two amphiboles in the other formed in equilibrium. Hornblende and gedrite, however, occur in the same shell and probably formed under similar conditions. The slight, but consistent differences in Al/Si ratios shows furthermore that these elements were partitioned between the two amphiboles. Since the Al and Si are the least mobile components, it is concluded that the hornblende and gedrite indeed formed in equilibrium and are truly coexisting.

Inspection of analytical data on coronas in the Artfiillet gabbro and dolerites (Fig. 2) shows why gedrite occurs in coronas in olivine-dolerite 158. In the gabbro and most dolerites the coronas consist of orthopyroxene, hornblende and spinel; one dolerite contains only orthopyroxene and hornblende; and dolerite 158 contains orthopyroxene, hornblende and gedrite. Apparently the bulk composition of the reactants proceeds from the three-phase triangle orthopyroxene-hornblende-spinel across the orthopyroxene-hornblende tie line into the three-phase triangle orthopyroxene-hornblende-gedrite. The position of the plagioclase in dolerite 158 at the Na-rich end of the compositional spectrum in gabbro and dolerites (Fig. 2), suggests that the change in mineralogy is mainly a function of plagioclase composition. The data in Figure 2 indicate, however, that gedrite formation in a corona is not simply due to higher Na/(Na + Ca) in plagioclase than in hornblende. Hornblende-spinel symplectites in coronas (diamonds, Fig. 2) possess the same Al/(Al + Si) ratio as the original plagioclase, but their Na/(Na + Ca) ratio is consistently lower. The hornblende-spinel tie lines pass plagioclase at lower Na/(Na + Ca) ratios. Consequently, either Na is lost or Ca gained during corona formation. This may be related to the alteration of augite to hornblende, since this requires addition of Na or loss of Ca. Open-system reaction with regard to Na and Ca must have occurred for the gedrite-bearing corona too, because closed-system reaction would yield ca. 25% gedrite in the amphibole shell, which is much more than the amount actually present (<10%). It is concluded, therefore, that gedrite may form in coronas when an excess amount of Na is present, taking account of all reactions in the rock that involve Na and Ca and not only corona formation.

Discussion

Comparison of the gedrite in the corona with published analyses of orthoamphiboles (references in Robinson et al., 1982) shows that it is highest in Na and Al of all orthoamphiboles coexisting with hornblende. Only the gedrites of Berg and Wiebe (1978) and of Schumacher (1980) (cf. also Robinson et al., 1982) extend to comparable or higher Na and Al, but do not occur together with hornblende. Figure 3 shows available data on coexisting orthoamphiboles and hornblendes. Due to the presence of a solvus between anthophyllite and gedrite below ca. 600°C (Spear, 1980b) four different types of orthoamphiboles coexisting with hornblende may be distinguished: off-solvus anthophyllites, solvus pairs of anthophyllite and gedrite, supersolvus orthoamphiboles, and off-solvus gedrites. Because the position of the solvus depends on Fe/Mg ratio (Spear, 1980b), some spread occurs in the positions of the orthoamphibole solvus pairs. Only two
orthoamphibole–hornblende pairs have been found for which gedrite definitely lies off the solvus (this paper; Spear, 1980b). The pair of Hawthorne et al. (1980) may also have gedrite lying off the solvus, but this is difficult to judge because they do not report formation conditions. Their gedrite contains exsolved anthophyllite and must at least have intersected the solvus during cooling.

A remarkable feature of Figure 3 is the large spread in orthoamphibole compositions as opposed to the relatively constant hornblende composition, resulting in fanning of the tie-lines. This fanning is exaggerated by the orthoamphibole solvus, but is present even for off-solvus and supersolvus orthoamphiboles. In the two most aluminous gedrites this fanning has proceeded so far that the AlIV content of Na in the orthoamphiboles increases, varying from a vacant A-site in anthophyllite to an almost completely filled A-site in the corona gedrite. Apparently orthoamphibole is much more flexible than hornblende with regard to Al contents and the occupation of the A-site.

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