Motion and metamorphism – Reaction rims

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Abstract

Reaction rims resulting from the partial reaction of two neighboring grains preserving a disequilibrium in the rock. Microstructures such as coronas and symplectite are the consequence. Reaction rims are a typical product of retrogression but samples from prograde metamorphism are also known. Coronas often consist of hydrous phases such as sericite, chlorite and serpentine. Symplectites were commonly made by solid – solid – reactions. They may also be produced by polymorphic reactions. Reaction rims preserve a disequilibrium in the rock because the run of the reaction was hindered by low diffusivities or the reaction starts only at preferred nucleation sites (dislocations, stacking faults, grain boundaries). Deformation has several effects on the run of metamorphic reactions. It may enlarge lattice diffusivities in strained crystals and allows or enlarges the access of H₂O to the rock due to reduced grain sizes and increases therefore the reaction rates. Reaction rims are used in reconstructing p – T – t – paths. Myrmekites are shear sense indicators.
## Contents

1. Introduction .............................................. 1
2. Typical microstructures .................................. 1
3. Common mineral reactions ............................... 4
4. Creation and preservation of reaction rims – the role of reaction kinetics ........................................... 6
5. The role of deformation during metamorphic transformations ......................................................... 8
6. Reasons for studying reaction rims ...................... 9
1. Introduction

Reaction rims are developed around grain boundaries, resulting from a partial replacement of one (or some) mineral phase by another (or some other, fig.1).

![Fig.1: principle sketch of a reaction rim, developed between the black and the gray phase (redrawn from Passchier and Trouw, 1998)](image)

Reaction rims are typical products of retrogression, but examples from prograde metamorphic reactions are also known. As a clear sign of disequilibrium between the involved phases they are good tools in reconstructing p – T – t – paths. Their thickness typically varies between 0,1 and 1 mm (Ashworth and Sheplev 1997).

In this paper are microstructures, mineral reactions, reaction kinetics and relations to tectonic movement discussed.

2. Typical Microstructures

Coronas

Coronas are shells surrounding a crystal of another composition consisting of one or several phases. The mineral layers are commonly sharp defined. Their mineralogy and the sequence of their layers is the consequence of the composition of the involved phases, the p – T – conditions during grow and the reaction kinetics, especially the presence of H$_2$O (Rubie 1990). Monomineralic coronas are called moats (fig. 4 pg.2).

As products of retrogression they typically consists of hydrous phases (sericite, chlorite or other; Barker, 1998). Coronas are well visible around porphyroblasts that are in disequilibrium with matrix phases. They are also created by the breakdown of single crystals due to changing p – T – conditions.

Atoll structures are possibly a special type of coronas. They consist of a mostly monomineralic ring surrounding a mixture of several other phases that normally doesn’t show a preferred orientation.

![Fig. 2: atoll garnet; LPL; width of view 1,5 mm Meall Druidhe, Kinloch Rannoch, Scotland (Yardley et al. 1992)](image)
The creation of atoll structures is under discussion. Atoll garnets (fig. 2) are thought to grow as coronas around biotite or cordierite with a later replacement of the core minerals by muscovite/chlorite and other phases (Passchier and Trouw, 1998).

**Double coronas** may be created by several mechanisms (Passchier and Trouw, 1998):
- Reaction between the core and the first corona.
- Reaction between the first corona and matrix minerals
- Breakdown of the core by another reaction, without involving the first corona

The outer rim is not always the youngest.

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**Fig. 3:** coronas of serpentine surrounding olivine; peridotite, Oberdielen/Hesse; XPL; width of view 5.5 mm
(Pichler and Schmidt – Riegraf 1993)

**Fig. 4:** muscovite moat around staurolite; width of view 14 mm; staurolite biotite schist; Pyrenees, ESP (Passchier and Trouw, 1998)

**Fig. 5:** complex corona surrounding olivine; the outer corona consists of a symplectitic intergrowth of clinopyroxene and plagioclase with a small outer rim of garnet, the inner one of fibrous orthopyroxene; brown grains are relics of plagioclase;
left: LPL; right: XPL; width of view 1,1 mm; granulate faciel olivine – dolerite; Midøy, NOR (Yardley et al. 1992)
Symplectite

A lamellar intergrowth of two or sometimes more phases is called *symplectite* (fig. 3). It mainly occurs in high-grade metamorphic rocks (especially granulites) as product of retrogression. A symplectite consists of rod – or worm – shaped, elongated grains that are roughly perpendicular orientated to the reacting interfaces. If a symplectite is affected to grain boundary area reduction, the grains may be more globular shaped (*globular symplectite*). The texture is thought to be the result of fast nucleation and the lack of fluid during growth. So its growth rate is mainly controlled by grain boundary diffusion (see chapter 4) and the spacing of the symplectite depends on the range of the slowest diffusing component (Barker, 1998). If a solid solution is cooled to its solvus, it may be formed an *exsolution symplectite*, when:

- Two identical solid solutions are not separated by grains of another chemical composition
- These grains have a different crystallographic orientation
- Diffusion is possible

This leads to the migration of the grain boundary into one of the grains leaving a symplectite behind.

The coarse symplectite of the double corona in fig. 6 is thought to grow first by the reaction:

(1)  \[ \text{Hbl} + \text{Gt} \Phi \text{Opx} + \text{Pl} \]

The fine-grained (younger) one was made by a breakdown of garnet:

(2)  \[ \text{Gt} \Phi \text{Opx} +\text{Pl} +\text{Spl} \]

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*Fig. 6:* double corona with a symplectitic internal structure between garnet (right) and hornblende (left); explanations in the text; LPL; width of view 6.5 mm (Passchier and Trouw, 1998)
3. Common mineral reactions

Every metamorphic transformation may produce reaction rims but examples from prograde reactions are rare.

Polymorphic reactions

Well-studied polymorphs are the Al$_2$SiO$_5$ – and SiO$_2$ – modifications. In both systems is recrystallisation necessary by creating the other modification. Nucleation at the interface of the instable modification or somewhere else in the rock is possible in case of phase changes in the Al$_2$SiO$_5$ – system. This may produce coronas (even as result of prograde metamorphism as shown in fig.7) or rocks containing two modifications at different sites.

![Fig. 7: topotactical replacement of andalusite (blue) by sillimanite (yellow) as result of uncompleted prograde metamorphism; XPL; width of view 4 mm; Mt. Stuart, Northern Cascades, WA; USA (Yardley et al. 1992)](image1)

![Fig. 8: chlorite replaces biotite; LPL; width of view 3 mm; coast of the Baltic Sea near Kiel (Pichler and Schmidt – Riegraf (1993)](image2)

Reletic coesite (fig. 9) is preserved as inclusions in garnet with partial replacement by quartz at cracks and grain boundaries. The developed quartz has a characteristic radial growth (Chopin 1984). The surrounding garnet shows radial cracks due to the volume rise during recrystallisation.

![Fig. 9: recrystallized quartz surrounding coesite; Left: LPL; well visible are the radial cracks in the garnet resulting from volume rising during the transformation Right: XPL; the typical radial structure of the grown quartz; width of view 1 mm; pyrope – coesite – quartzite; Dora Maira Massif, ITA (Chopin, 1984)](image3)
Chloritisation

In case of retrogression, chlorite may develop by the breakdown of biotite (fig. 8, pg. 4), garnet, cordierite, green hornblende and other minerals. The precise nature of the reaction depends on the bulk rock composition but aqueous fluids are always involved.

Sericitisation

Sericitisation occurs under the influence of water rich fluids. It is common in quartzofeldspathic rocks and metapelites, involving plagioclase, K – feldspar, staurolite cordierite and Al$_2$SiO$_5$ – polymorphs. The product of the reaction is a fine-grained aggregate of white mica. The alteration of K - feldspar is shown as example:

(1) Kfs + H$^+$ Φ Ser + SiO$_2$ + K$^+$
3 K[AlSi$_2$O$_8$] + 2 H$^+$ (aq) Φ KAl$_2$[(OH)$_2$/AlSi$_3$O$_{10}$] + 6 SiO$_2$(aq) + 2K$^+$ (aq)

Pinnitisation

Pinnite is the most common retrogression product of cordierite due to the reaction with an aqueous fluid:

(2) Crd + K$^+$ + H$_2$O Φ Chl + Mv
This leads to a fine-grained yellow mixture of sericite and/or chlorite and biotite (fig 5).

Serpentinisation

Serpentine is the most common alteration product of ultramafic rocks. Serpentinitisation (fig. 4) mainly occurs in three geological settings: in the mantle itself, by ocean floor metamorphism and during uplift in orogenic belts by the following simplified reactions:

(3) Fo + fluid Φ Srp
3 Mg$_2$[SiO$_4$] + SiO$_2$(aq) + 2 H$_2$O Φ 2 Mg$_3$[(OH)$_2$/Si$_2$O$_5$)]
SiO$_2$ is added to the system by the breakdown of the fayalite – component:

(4) Fa + O$_2$ Φ Mag + SiO$_2$
3 Fe$_2$[SiO$_4$] + O$_2$ Φ 2 Fe$_3$O$_4$ + 3 SiO$_2$(aq)

The created magnetite commonly nucleates at preexisting chromites. Orthopyroxene is also transformed into serpentine:

(5) En + H$_2$O Φ Srp + SiO$_2$
3 Mg$_2$[Si$_2$O$_6$] + 4 H$_2$O Φ 2 Mg$_3$[(OH)$_2$/Si$_2$O$_5$)] + SiO$_2$(aq)

(6) Fs + O$_2$ Φ Mag + SiO$_2$
3 Fe$_2$[Si$_2$O$_6$] + O$_2$ Φ 2 Fe$_3$O$_4$ + 6 SiO$_2$(aq)

Most of the released SiO$_2$ is fixed by reaction (3), the remaining one is normally taken out of the system because the created serpentinite contains commonly no SiO$_2$ – modification.
Kelyphitic rims

The term kelyphitic rim is used in two different ways (Barker 1998):

1. For a symplectitic intergrowth of pyroxene and spinel surrounding olivine especially in gabbros as product of the reaction

\[
\text{(7) } \text{OL} + \text{Pl} \quad \Phi \quad \text{Opx} + \text{Cpx} + \text{Spl}
\]
\[
2 \ (\text{Mg,Fe)}_2(\text{SiO}_4) + \text{Ca}[\text{Al}_2\text{Si}_2\text{O}_8]
\]
\[
\Phi (\text{Mg,Fe)}_2(\text{Si}_2\text{O}_6) + (\text{Mg,Fe})\text{Ca}[\text{Si}_2\text{O}_6] + (\text{Mg,Fe})\text{Al}_2\text{O}_4
\]

2. In a generalized way for coronas showing a symplectitic internal structure, for example:

- Hornblende/pyroxene – spinel – symplectite surrounding pyrope – rich garnet especially in mantle rocks

Myrmekite

A symplectitic intergrowth of quartz and plagioclase replacing K – feldspar in metamorphic and igneous rocks is called myrmekite. It normally grows at sites of high stress and therefore it is mainly concentrated in shortened parts of the deformed K - feldspar crystal (Passchier and Trouw, 1998).

4. Creation and preservation of reaction rims – the influence of reaction kinetics

If the rock in fig. 10 moves from position X to Z, crossing the reaction curve at Y, the phases A + B reacts theoretically to the phases C + D. But in reality the reaction needs not necessarily take place or runs incomplete because of the influence of reaction kinetics.

After reaching the reaction curve, phase Z starts to nucleate. This mainly occurs at grain defects such as dislocations, stacking faults, grain boundaries and others because the energy associated with defects contributes to the energy required for creation a nucleus with a significant size (Rubie and Thompson 1985).
For solid – solid – transformations the rate equation for homogenous nucleation can be written as (Rubie 1998):

\[(E1) \quad N = K_0 T \exp(-\Delta G^*/kT) \cdot \exp(-\Delta H_a/RT)\]

with \(\Delta G^* = 16\pi\gamma^3/3(\Delta G_v + \varepsilon^2)\)

The symbols stand for:
- \(N\) nucleation rate
- \(K_0\) a constant
- \(T\) temperature
- \(\Delta G^*\) activation energy
- \(k\) Boltzmann constant
- \(-\Delta H_a\) activation enthalpies for growth
- \(R\) gas constant
- \(\gamma\) interfacial energy
- \(G_v\) free energy change
- \(\varepsilon\) strain energy

Overstepping of the reaction curve is possible even in geological times until a significant number of nuclei have been created. The magnitudes of strain (\(\varepsilon\)) and interfacial energy (\(\gamma\)) control the width of overstepping because the free energy change (\(-\Delta G_v\)) has to balance them (Rubie 1998). If products and reactants have similar lattices and the nucleation takes place at the interface of the reactant, the possible overstepping may be smaller due to low interface energies (analog leading different lattices to higher ones). A high number of products may also induce larger oversteps (Rubie 1998). The presence of \(H_2O\) increases the rate of nucleation even in case of a solid – solid – reaction.

The effects discussed above may lead to inhomogeneous, slow or not occurring nucleation and may therefore preserve disequilibrium in the rock. The influence of strain on nucleation is responsible for the creation of myrmekites and it is possible that this effect leads in a similar way to the creation of other reaction rims.

The nucleation creates a chemical potential gradient in the rock that drives diffusion. Because a metamorphic reaction is either heat flow (in case of devolatilisation), interface (short period after nucleation and nucleation itself) or diffusion (the most metamorphic reactions) controlled (Tracy and McLellan 1985), diffusivities has an important role in the preservation of reaction rims:

According to Fick’s first law

\[(E2) \quad J_i = -D_i \frac{dc_i}{dx}\]

the flux \(J_i\) of the components depends on the chemical potential gradient \(dc_i/dx\) and the diffusivities \(D_i\). In order to get small reaction rates of a diffusion-controlled reaction, the diffusivities or the chemical potential gradient has to be small. In case of metamorphism the occurring chemical potential gradient is not known but there are a lot of experimental data available for diffusivities.

Three possibilities are discussed here:
- Lattice diffusion
- Grain boundary diffusion
- Diffusion in a fluid

**Lattice diffusivities** are very low; the resulting replacement is even in geological times nearly insignificant especially at lower temperatures. The range of the components is normally not larger than some millimeters.

**Grain boundary diffusivities** are about \(10^4\) magnitudes higher. The components may be moved over a distance of some meters. Grain boundaries are the consequence of crystallographic mismatch and misorientation between two grains bordering on each other. Their width (\(\delta\))
may be only two atom diameters (the area of crystallographic misorientation) but the breath used for component transport is on the nanometer scale (Barker and Zhang 1998). A fluid allows the transport of components over large distances and the diffusivities are much higher as those described above. Nevertheless the access of H\textsubscript{2}O to the rock increases the reaction rates some eight to ten times by comparation with the dry rock (Rubie 1998) even in case of solid – solid - reactions.

The breakdown of hydrous phases causes the presence of fluid during prograde metamorphism and the resulting high reaction rates are the reason why reaction rims are seldom produced under such environments. At the p – T – peak most or all H\textsubscript{2}O had left the rock (especially in case of granulites and eclogites) and retrograde reactions run slow or are impossible because of the very low lattice diffusion rates. This kinetically effect causes the uncompleted reactions that left reaction rims.

Grain boundary diffusion is a little bit faster and is especially considered by the forming of symplectites. It even explains the growth of coronas consisting of hydrous phases (Ashworth, 1993) that are probably not grown under the influence of a fluid: A fluid circulates at fractures and leads therefore to an inhomogeneous distribution of the product as it is typical for completely alterated rocks even at the scale of thin sections. But the distribution of reaction rims is mostly homogenous over a larger scale (fig. 4 pg. 3).

5. **The role of deformation during metamorphic transformations**

Unfortunately, there aren’t many experimental data available (Kramer and Seifert; 1991) but a few points are discussed here.

*Strained crystals*

High dislocation densities increase the diffusivities of an unstrained crystal only a little bit according to experiments and theoretically models (Rubie and Thompson 1985). Low to medium stresses allows the moving of dislocations in a crystal lattice (dislocation creep; Barker, 1998). Therefore increases the diffusivity along the cores of the dislocations (pipe diffusion). Diffusive transport in these created paths is called *strain-enhanced diffusion*. From experimental data the following equation was derived (Kramer and Seifert, 1991):

\[
D_s/D_l = 1 + B[T] \ast >
\]

The symbols stand for:

- \(D_s\) strain enhanced diffusivity
- \(D_l\) lattice diffusivity
- \(B[T]\) the measure of diffusive sensitivity of strain rate; it strongly depends on temperature
- \(>\) strain rate

Equation (E3) shows that the higher the strain rate the higher the strain enhanced diffusivity. Therefore a strained crystal allows higher lattice diffusivities and leads to higher reaction rates if the reaction is diffusion controlled.

The nucleation on defects is energetically more favored in a strained lattice as discussed in chapter four.
Grain size reduction

Tectonically movement decreases the grain size of the rock in a brittle or ductile way. That has the following effects:

- A reduced grain size leads to higher grain surfaces and therefore to higher reaction rates.
- The time for a complete reaction is proportional to the square of the grain diameter (Rubie and Thompson 1984) and therefore the complete transformation is reached earlier.
- Deformation, especially in a brittle way, may enlarge permeability due to reduced cracks and reduced grain sizes. Barker and Zhang (1998) discuss the effect of grain – boundary dilatancy: the breath of the grain boundary may increase under the influence of stress.
- A reduced grain size increases the grain boundary diffusivity and the number of possible nucleation sites due to a higher grain boundary area per given volume (Rubie 1990).
- The reacting components have to be transported over lower distances.

Other points

- Stress gradients may increase chemical potential gradients and hence according to Fick’s first law (E2) the rate of diffusive mass transfer.
- Dynamical recrystallization is a way to allow phase changes.

Conclusions

The processes discussed above allow or enlarges the access of fluid to the rock. An increasing $p_{\text{H}_2\text{O}}$ starts or accelerates hydratisation reactions such as sericitisation and chloritisation. The presence of a fluid leads too much higher diffusion rates over larger distances and $\text{H}_2\text{O}$ takes effect as catalyst on some reactions.

Under such conditions the rock is mostly completely altered and reaction rims lack and therefore tectonically movement is effective against their preservation.

6. Reasons for studying reaction rims

Reaction rims may be studied with a light microscope if they are large enough. Very fine-grained symplectites require the use of an electron microscope or a microprobe.

(1) From reaction rims is known which mineral reactions exist which are widespread or rare.

(2) Myrmikites are used as shear sense indicators (fig. 11) due to their creation at sites of high differential stress. Internal structures (quartz lamellae) are another independent one.
3) Reaction rims can be used in reconstructing p–T–t– paths:
The phases D + C (fig. 10 pg. 7) resulting from the younger incomplete reaction $A + B \Phi C + D$ and the phases $A + B$ are relics of a former higher-grade assemblage. Therefore can be considered that the rock moves through the stability field of $A + B$ and afterwards through that of $C + D$. If the stability fields are small enough, the p–T– path of the rock might be relative exactly calculated.

4) Exsolution symplectites are used as geothermometers due to the strong temperature dependence of exsolution. Well-studied pairs are orthopyroxene – clinopyroxene; calcite – dolomite; plagioclase – alkali feldspar and muscovite - paragonite
Appendix

Mineral abbreviations

The mineral abbreviations are taken from Kretz (1983) except those marked with * taken from Bucher and Frey (1994)

Bt biotite
Cpx clinopyroxene
Chl chlorite
Chr chromite
Crd cordierite
En enstatite
Fa fayalite
Fo forsterite
Fs ferrosilite
Grt garnet
Kfs K – feldspar
Mag magnetite
Ms muscovite
Ol olivine
Opx orthopyroxene
Pl plagioclase
Prp pyrope
Qtz quartz
Ser* sericite
Srp serpentine
Spl spinel
St staurolite

Other abbreviations

LPL linear polarized light
XPL crossed polarized light
References


Chopin, C; (1984): Coesite and pure pyrope in high – grade blueschists of the western Alps: a first record and some consequences. – Contributions to Mineralogy and Petrology, 86, 107 – 118


