Mechanically- v. diffusion-controlled metamorphic microstructure: a symplectite example from Rhodope Metamorphic Complex (Greece)

Author(s):
Moulas, E.; Tajcmanova, L.; Vrijmoed, J. C.; Podladchikov, Y.

Publication Date:
2015

Permanent Link:
https://doi.org/10.3929/ethz-a-010741621

Originally published in:
Journal of Metamorphic Geology 33(8), http://doi.org/10.1111/jmg.12141

Rights / License:
In Copyright - Non-Commercial Use Permitted
Mechanically– versus diffusion–controlled metamorphic microstructure: A symplectite example from Rhodope Metamorphic Complex (Greece)

MOULAS E.\textsuperscript{a}, TAJČMANOVÁ L.\textsuperscript{a}, VRIJMOED J.C.\textsuperscript{a} AND PODLADCHIKOV Y.\textsuperscript{b}

\textsuperscript{a} Department of Earth Sciences, ETH Zurich, Switzerland \\
\textsuperscript{b} Institute of Earth Sciences, University of Lausanne, Switzerland

Correspondence email: evangelos.moulas@erdw.ethz.ch

Short title: Grain–boundary diffusion in plagioclase rim

\textbf{ABSTRACT}

Gradients in chemical potential are the driving force for chemical diffusion and their spatial distribution is thus essential to investigate equilibrium in metamorphic rocks. At high temperatures (>650ºC), where chemical diffusion is relatively fast, the development and preservation of compositional zoning in minerals can be controlled by mechanically maintained pressure variations. Therefore, the dependence of chemical potentials on pressure plays an important role in correct interpretations of rock microstructures. Distinguishing between pressure–controlled chemical zoning and zoning reflecting chemical diffusion is a challenge. To tackle this challenge, we investigate a symplectitic microstructure around kyanite in an amphibolitized eclogite from the Rhodope Metamorphic Complex (Greece). The sample recrystallized at high temperatures (~720ºC) and low pressures (P<1GPa) during which kyanite was replaced by fine–grained symplectites of sapphireine, spinel, plagioclase and corundum. The plagioclase rim around kyanite shows a cusp–shaped chemical zoning of calcium along the grain boundaries. The results from a combined phase equilibria and diffusion modelling show that the cusp–like shapes were developed by fast grain boundary diffusion at constant pressure after the relaxation of grain-scale pressure variations across the plagioclase rim. The results illustrate an example where petrographic observations help distinguishing between mechanically–and diffusion–controlled chemical zoning.

Keywords: Chemical diffusion, chemical zoning, grain–boundary diffusion, pressure variations, unconventional barometry
INTRODUCTION

Gradients of pressure, temperature and chemical potential \((P, T, \mu)\) drive transport phenomena such as thermal and chemical diffusion (e.g. Lebon et al., 2008). Chemical zoning preserved in metamorphic minerals is commonly interpreted as a result of slow chemical diffusion leading to apparent disequilibrium microstructures (c.f. Carlson, 2002). In such microstructures, the equilibrium length scale is smaller than the size of the considered system. In most petrological studies, the system under consideration ranges from micrometer to centimeter scale. On this scale, variations in mineral compositions impose variations in the chemical potentials of the respective components. Chemical equilibrium is established when chemical potential gradients have vanished by chemical diffusion. Such a view is generally valid under the assumption of constant pressure and temperature throughout the system. The preservation of grain–scale pressure and stress gradients has been well documented for pressurized inclusions (Parkinson & Katayama, 1999; Enami et al., 2007; Barron et al., 2008; Howell et al., 2010). Interestingly, residual stress (>0.3GPa, locally up to 0.8GPa) has been recently estimated from strain measurements in quartz fragments of a cataclasite (Chen et al., 2015). Different mechanical models for different rheology have been suggested and they document the feasibility of maintaining the pressure gradients on a grain scale (Gillet et al., 1984; Tajčmanová et al., 2014; Dabrowski et al., 2015). Such pressure variations lead to the development of chemical potential gradients, even if the chemical composition of a mineral is homogeneous. These gradients of chemical potential drive chemical diffusion which leads to the development of compositional zoning in chemical equilibrium (Tajčmanová et al., 2015). Recently, Tajčmanová et al. (2014) developed a barometric method for chemically zoned minerals under pressure variations. This unconventional barometry can be applied to microstructures where relaxation of pressure is significantly slower than chemical diffusion, i.e. the microstructures are mechanically controlled. Therefore, it is necessary to identify when a microstructure is mechanically– or diffusion–controlled.

In this work, we examine the limits of the applicability of the unconventional barometer proposed by Tajčmanová et al. (2014) on a microstructure from an amphibolitized eclogite sample from Rhodope Metamorphic Complex (Greece). The microstructure is similar to those observed in granulites from the Bohemian Massif where chemically zoned plagioclase rims developed around kyanite during decompression (Tajčmanová et al., 2007, 2011, 2014; Štípská et al., 2010). Tajčmanová et al. (2014) interpreted the chemical zoning in such a plagioclase rim as a result of pressure variation developed across the rim. On the contrary, the petrographic evidence of low pressure symplectites after kyanite in the Rhodope sample points to a pressure relaxation at the time of final re–equilibration. Furthermore, the microstructure also shows characteristics of active chemical transport inside the plagioclase along the grain boundaries. Assuming that the observed compositional pattern represents chemical equilibrium, the pressure variation derived by the unconventional barometry is not consistent with the view that grain boundaries are weak material interfaces. Therefore, we develop a two–dimensional numerical model for chemical diffusion in the plagioclase rim around symplectitized kyanite. The results indicate that grain boundary diffusion is a mechanism responsible for the development of the compositional pattern that is observed in the plagioclase rim. This example is complementary to the results of Tajčmanová et al. (2014) and it provides microstructural evidence that help to distinguish between mechanically–maintained and diffusion–limited chemical zoning.

SAMPLE DESCRIPTION

The investigated sample originates from the Rhodope Metamorphic Complex (N. Greece–S. Bulgaria) (Burg, 2012). Peak-pressure conditions reported for this sample are \((700—720^\circ\text{C} and 2.0—2.2\text{GPa};\) Liati & Seidel, 1996). The kyanite eclogite sample experienced re–equilibration in upper–amphibolite–
facies conditions (~720°C and 0.4—0.5 GPa) during decompression (Moulas et al., 2013a). For a detailed petrographic description of the whole sample and a description of the analytical methods see Moulas et al. (2013a).

The high–pressure assemblage is characterized by garnet and omphacitic pyroxene. The matrix is composed of diablastic amphibole and amphibole + plagioclase ± diopside symplectites (Fig. 1a). These matrix symplectites are indicators of omphacite replacement at low pressures (Boland & van Roermund, 1983). Kyanite was part of the eclogite–facies mineral assemblage that was progressively replaced by a low–pressure assemblage. The kyanite is surrounded by a zoned plagioclase rim with high (molar) anorthite component ($X_{An}=0.40$) at the kyanite/plagioclase interface (Fig. 2). The anorthite component decreases towards the quartz–bearing matrix ($X_{An}=0.08$; Fig. 2b). In addition, plagioclase is anorthite rich in the regions adjacent to the grain boundaries (Fig. 2a,c). The compositional contours of the anorthite component in the vicinity of grain boundaries are cusp shaped and they are pointing towards the matrix (Fig. 2c). Symplectites of spinel + plagioclase + corundum, occasionally containing sapphirine replace the kyanite relics (Fig. 1c,d), see also (Liati & Seidel, 1994, 1996). In most of the microstructures, the replacement of kyanite by the low–pressure assemblage was complete and only pseudomorphs after kyanite can be observed (Fig. 1d). In some cases, kyanite was not totally replaced but it was completely surrounded by spinel + plagioclase + corundum ± sapphirine (Fig. 1c). The thickness of the symplectites around kyanite is variable and the composition of plagioclase in these symplectite zones (intergrowths around kyanite) is nearly homogeneous (Fig. 2a). Plagioclase symplectites in the pseudomorphs after kyanite are generally richer in anorthite ($X_{An}>0.30$) compared to the plagioclase symplectites in the matrix ($X_{An}<0.30$). Although plagioclase is always present in the kyanite pseudomorphs, the distribution of spinel and sapphirine seems to be controlled by local compositional variations (Fig. 1d; see also Moula. al. 2013a).

THE CAUSE OF CHEMICAL VARIATION ACROSS THE MICROSTRUCTURE

Similar plagioclase rims to the one shown in Fig. 1b have been described by Tajčmanová et al. (2007, 2014) from granulite samples from the Bohemian Massif. These authors suggested that the plagioclase rim around kyanite represents a mechanical barrier which isolated it from the lower–pressure matrix and thus preserved kyanite at high pressure (Tajčmanová et al., 2007, 2014). Such a mechanical shell thus served as a naturally–formed multi–anvil cell which maintained a pressure gradient between the kyanite and the low–pressure matrix (Tajčmanová et al., 2014). The pressure variation can lead to the chemical redistribution of albite and anorthite components in the plagioclase rim around kyanite, i.e., from anorthite–rich plagioclase next to kyanite to anorthite–poor plagioclase next to the matrix. Tajčmanová et al. (2014) proposed that mechanically imposed pressure variations maintained the chemical zoning in plagioclase at high temperatures. However, the fact that the multi–anvil model is mechanically feasible does not imply that every multi–grain rim will maintain grain–scale pressure variations. Recent studies on host–inclusion systems with non-linear viscous rheology (e.g. Dabrowski et al., 2015) suggest that it may take several Ma to relax the pressure variations. In the case pressure gradients have vanished, the application of the unconventional barometry on compositional zoning proposed by Tajčmanova et al. (2014) is inappropriate.

The similar plagioclase rim around kyanite from the Greek Rhodope provides a suitable texture for using the unconventional barometry to test the hypothesis that chemical zoning is maintained by pressure variations. Applying the barometry to the zoned plagioclase rim from Rhodope shows that pressure is highest next to kyanite as well as at the grain boundaries within the multi–grain plagioclase rim (Fig. 3). In addition, the replacement of kyanite by the low–pressure assemblage of spinel + corundum + plagioclase ± sapphirine (Fig. 1c,d) indicates that pressure was low on both sides of the
plagioclase rim at the time of the symplectite formation (Fig. 4a; Moulas et al., 2013a). In the context of the multi–anvil cell model of Tajčmanova et al. (2014), the weak grain boundaries should record lower pressure than the rest of the plagioclase grains (Fig. 3c of Tajčmanova et al., 2014). Therefore, the results of the unconventional barometry (Fig. 3) and the P–T conditions inferred from local thermodynamic equilibrium (Fig. 4) show that the high anorthite composition observed adjacent to the plagioclase grain boundaries was not generated by pressure variations.

MODELLING GRAIN BOUNDARY DIFFUSION

Diffusion Modelling

To understand the mechanism leading to the formation of the anorthite–rich cusps, we developed a numerical model that simulates diffusion in plagioclase as well as along the grain boundary. The high content of anorthite along the grain boundaries in the plagioclase rim shows that Ca was preferentially transported along these boundaries. Grain boundary diffusion involving diffusivities several orders of magnitude higher than the volume diffusion within the grains is a mechanism that explains such a feature (c.f. Fisher, 1951; Whipple, 1954; Le Claire, 1963; Joesten, 1991). The grain boundary is considered to be isolated and is treated as a zone of finite thickness and higher diffusion coefficient (c.f. Canon & Stark, 1969; Dohmen & Milke, 2010). Therefore, a morphologic characteristic of grain boundary diffusion is the formation of penetrating cusp–shaped compositional isopleths (Le Claire, 1963; Keller et al., 2008; Marquardt (née Hartmann) et al., 2011) with the cusp pointing in the direction of mass transport (e.g. Kaur et al., 1995).

The model developed for the plagioclase rim in Fig. 2 is characterized by two zoned plagioclase grains separated by a grain boundary (Fig. 5a). Different numerical approaches have been used by various authors in order to quantify grain boundary diffusion in isolated grain boundaries. The approach of Fisher (1951) is the most commonly used one. It provides the solution for the diffusion of a component C (molar concentration) within and outside an isolated grain boundary. The evolution of the composition, exactly at the grain boundary and outside of it, is given by the following relationships:

\begin{equation}
\frac{\partial C}{\partial t} = D^{GB} \frac{\partial^2 C}{\partial x^2} + \frac{2D^V}{\delta} \left( \frac{\partial C}{\partial y} \right)_{y=0.5+\delta/2} \quad \text{for} \ y = 0.5 + \frac{\delta}{2} \\
\frac{\partial C}{\partial t} = D^V \left( \frac{\partial^2 C}{\partial x^2} + \frac{\partial^2 C}{\partial y^2} \right) \quad \text{for} \ y > 0.5 + \frac{\delta}{2}
\end{equation}

where t is time, x and y are the coordinates as in Fig. 5a, and \(\delta\) is the thickness of the effective grain boundary (Kaur et al., 1995; Dohmen & Milke, 2010). The coefficients \(D^{GB}\) and \(D^V\) are the diffusion coefficients for the grain boundary and the intra–granular region respectively. The diffusion coefficients in the approach of Fisher (1951) are treated as constants (isotropic and independent of composition) and the diffusion is Fickean (Kaur et al., 1995). The modelling of diffusion of major components in plagioclase requires a different approach than that of Fisher (1951). Our approach considers that the grain boundary is a thin region where the diffusion coefficient is higher than the diffusion coefficient in the rest of the domain (\(D^{GB}>>D^V\)). The system of equations is shown below:
\[
\frac{\partial C}{\partial t} = -\left( \frac{\partial J_x}{\partial x} + \frac{\partial J_y}{\partial y} \right) \\
J_x = -D \frac{\partial C}{\partial x} \\
J_y = -D \frac{\partial C}{\partial y}
\] (2)

where \(J_x\) and \(J_y\) are diffusion fluxes. The diffusion coefficient \(D\) is equal to \(D_{GB}\) inside the thin grain boundary region and is equal to \(D^V\) outside of it. To check the validity of this approach, we consider a simple example of Fickean diffusion. For a sufficiently high numerical resolution (i.e. 300x300 for Fig. 5a), the results from two approaches are indistinguishable (Fig. 5b,c). Fickean diffusion is valid only for ideal solutions which is an oversimplification of the plagioclase solid solution. Therefore we follow the procedure outlined in Tajčmanová et al. (2015) for diffusion in binary plagioclase and utilize the second approach as it already compatible with variable diffusion coefficients. In a binary system, only one composition is independent and the conservation of mass for a binary plagioclase is (De Groot & Mazur, 1962):

\[
\rho \frac{d(C_{Ab})}{dt} = -\nabla J_{Ab}
\] (3)

where \(\rho\) is density \(C_{Ab}\), is the mass fraction of albite in plagioclase, \(t\) is time and \(J_{Ab}\) is the flux of mass of the albite component. For consistency with Fickean diffusion in the dilute limit, the flux \(J_{Ab}\) has to be equal to:

\[
J_{Ab} = -\frac{\rho}{RT} D C_{Ab} C_{An} M_{pl} V (\mu_{Ab} - \mu_{An})
\] (4)

(Eq. 30, Tajčmanová et al., 2015) where \(D\) is the diffusion coefficient with units of \((m^2 s^{-1})\), \(C_{Ab}\) and \(C_{An}\) are the mass fractions of albite and anorthite respectively, \(R\) is the universal gas constant, \(T\) is temperature and \(\mu_{Ab}, \mu_{An}\) are their chemical potentials respectively in units of J kg\(^{-1}\). The factor \(M_{pl}\) is the molecular weight of the plagioclase solution. The ratio \(D_{GB}/D^V\) is commonly greater than \(10^4\) at metamorphic temperatures (Joesten, 1991) and so a \(10^3\) ratio was chosen as a minimum estimate. As \(M_{pl}\) and the chemical potentials are functions of the plagioclase composition, the effective diffusion coefficient is also composition dependent.

In the model, different types of boundary and initial conditions have been considered. The albite concentration at the plagioclase–matrix interface is considered constant through time (Dirichlet boundary condition) because the fine–grained polycrystalline matrix acts as an infinite reservoir. Plagioclase in contact with kyanite (left boundary in Fig. 5) may have either (i) constant composition time or (ii) zero flux (Neumann boundary condition). The upper and lower limits of the plagioclase grains in the model domain have been considered to be far away from the grain boundary. Two
different types of initial conditions can be assumed for the compositional distribution in the plagioclase grains: (1) an initially zoned composition profile and (2) a constant composition (flat chemical profile). The compositionally zoned profile follows the $C_{An}$ trend unrelated to the grain boundaries (Fig. 2b). The chemical potentials of albite and anorthite components in plagioclase are calculated using the thermodynamic database of Holland & Powell (1998; revised 2003) and the feldspar solution model of Fuhrman & Lindsley (1988). The evolution of the plagioclase composition through time is estimated numerically via an explicit finite–difference scheme (e.g. Gerya, 2010).

For a compositionally zoned initial condition and Dirichlet boundary conditions, a Ca–rich zone develops in the vicinity of the grain boundary (Fig. 6a,b). This Ca–rich zone forms a cusp–like shape which is asymmetric (using a vertical axis of symmetry) and points towards the matrix side of plagioclase rim. This observation is also in agreement with experimentally–produced textures (Marquardt (née Hartmann) et al., 2011) where the source of the diffusing component acts as an infinite reservoir. For the case of Neumann left–boundary condition (Fig. 6c,d), the cusp shape of the compositional contours is more symmetric (i.e. axis of symmetry is vertical at $x \approx 0.03$mm in Fig. 6c). Under the absence of pressure gradients assumed here, diffusion does not occur for the case of an initially flat chemical profile. Under constant pressure, such a situation is considered as equilibrium and does not evolve in time.

**Reaction–diffusion modelling**

The results of the diffusion modelling show that to simulate the cusp–like compositional shape of the microstructure, a source of Ca is needed at the kyanite/plagioclase interface. This source can be external (i.e. outside the microstructure) or internal. In the external case, fluid–filled cracks acting as fast–diffusing pathways to supply the necessary Ca should be observed, but none was present. For the internal source, Ca should be obtained from the consumption of former plagioclase at the kyanite/plagioclase interface. The systematic presence of corundum and spinel at the kyanite/plagioclase interface (Fig. 2a) indicates that plagioclase is the only source of Ca in this microstructure. In addition, spinel and sapphire as the only Fe—Mg–bearing phases in the symplectite assemblage require an additional influx of Fe and Mg. Petrographic observations show that the source of these elements is local (Tajčmanová et al., 2011 ; Moulas et al., 2013a).

In order to investigate the possibility of having a local source of Ca due to a reaction at the plagioclase/symplectite interface, additional numerical calculations were performed (Fig. 7). In these simulations, the local source of Ca is the symplectite forming reaction on the kyanite–plagioclase interface (left side of Fig. 7). Only no–flux boundary conditions were considered to investigate the potential of locally sourced Ca. The reaction is approximated with a moving reaction front which consumes plagioclase and conserves Ca. Based on microstructural observations, the volume fraction of plagioclase after the reaction is reduced in half (Fig. 7). The velocity of the reaction front is taken constant (see caption of Fig. 8 for details). Plagioclase in the reacted zones forms fine–grained symplectites which have high surface to volume ratio and therefore the diffusion coefficient in plagioclase after the reaction is assumed equal to the one in the grain boundary. A high value for the diffusion coefficient in the reacted zone is supported by the relatively homogeneous composition of plagioclase in the reacted zone (Fig. 2a).

The numerical results of reaction coupled to diffusion show that the consumption of plagioclase is sufficient to produce the necessary Ca in order to produce the cusp–shaped isopleths of anorthite in plagioclase. The model results for the initially zoned grain are similar to the observed plagioclase composition (Fig. 8a,b). For the initially unzoned plagioclase, the concentration cusp is more pronounced but the zoning in the plagioclase grain is too sharp compared to the petrographic
DISCUSSION AND CONCLUSIONS

The increasing evidence of pressure and stress variations preserved on a grain scale (Moulas et al., 2013b and references therein; Chen et al., 2015) requires alternative views of rock microstructures. Pressure, as one of the most important thermodynamic variables, can significantly influence the chemical potentials across the rock microstructure, and as a consequence influence chemical diffusion (Tajčmanová et al., 2015). If pressure relaxation is much slower than diffusional homogenization, chemical zoning in minerals may record a spatial variation in pressure. The functional dependence of the chemical potential on pressure in a binary feldspar was used by Tajčmanová et al. (2014) to derive an unconventional barometer for plagioclase, and this was used to estimate the pressure gradient that had to be present in order to satisfy thermodynamic equilibrium. In theory, this implies that every zoned plagioclase crystal may represent a “fossilized” pressure gradient. Therefore, it is important to develop criteria to test the application of the unconventional barometry. For an appropriate application of the unconventional barometer, we investigated a plagioclase rim from Rhodope that resembles the plagioclase rims around kyanite from the Bohemian Massif used in Tajčmanová et al. (2014). The formation of low–pressure symplectite at the interface between kyanite and a plagioclase rim indicates that pressure was relaxed at both sides of the plagioclase rim, i.e. at the matrix and symplectite interface, at the time of symplectite formation. The multi–anvil model proposed by Tajčmanová et al. (2014) implies that pressure in the grain boundaries is low relative to the plagioclase grains. However, the unconventional barometry predicts high–pressure along the grain boundaries (Fig. 3). Therefore, the elevated anorthite concentration in grain-boundaries of the plagioclase rim cannot be explained by a mechanically–controlled zoning.

A new numerical model involving coupled reaction and diffusion with high diffusion coefficient along the grain boundary was developed to fit the observed compositional zoning pattern in the plagioclase from Rhodope. The numerical modelling of grain boundary diffusion indicates that a source of Ca is required on the kyanite–side of plagioclase in order to reproduce the observed concentration pattern in plagioclase. The model results fit the observations better when: i) plagioclase is initially zoned ii) Ca is produced locally through the consumption of plagioclase. This implies that the plagioclase rim must have been zoned before the growth of the low–pressure symplectite. Although it has been shown that the pressure variation is not required for the development of the compositional cusps in plagioclase, the relic plagioclase zoning across the plagioclase rim might represent a mechanically–controlled chemical zoning as described in Tajčmanová et al. (2014). The relaxation of such a pressure variation across the plagioclase rim and the pervasive formation of low pressure symplectites explains why kyanite is only rarely preserved in the studied samples. Our results attest to the importance of microstructural observations combined with phase equilibria and diffusion modelling to distinguish mechanically– from diffusion–controlled microstructures.

ACKNOWLEDGEMENTS

This study is supported by the ERC starting grant to L.T. (335577). Roger Powell and Dimitrios Kostopoulos are acknowledged for the initiation of fruitful discussions regarding these microstructures. This paper benefited from comments by Doug Robinson and an anonymous reviewer. Doug Robinson is particularly acknowledged for the editorial handling of this manuscript.
REFERENCES


Metamorphic Rocks.


**FIGURE CAPTIONS**

**Fig. 1**: Back-scattered images (BSE) showing the main microstructural features of the investigated sample. Mineral abbreviations are after Siivola & Schmid (2007). A detailed description of chemical compositions of all phases as well as details on the P–T evolution can be found in Mouls *et al.*, (2013a). (a) Amphibole+plagioclase+magnetite corona surrounding a garnet porphyroblast. Rutile and quartz are typical inclusions in the garnet porphyroblasts. The matrix constitutes mainly of diablastic amphibole and amphibole+plagioclase±clinopyroxene symplectites. (b) Kyanite crystal with a plagioclase rim. Symplectites of spinel occur at the kyanite-plagioclase interface. Note the cracks in the plagioclase rim. (c) Symplectites of spinel, corundum, plagioclase and occasionally sapphire replacing kyanite. The surrounding matrix is composed of clino–amphibole and plagioclase. (d) The symplectites of spinel, corundum, plagioclase and sapphire form a pseudomorph after kyanite.
Fig. 2: Chemically zoned plagioclase around kyanite. (a) Composition map of plagioclase around kyanite. Red colours correspond to high–anorthite content. The color map has been calibrated from spot analyses. Note the presence of spinel adjacent to kyanite. (b) Anorthite content across plagioclase rim. (c) Anorthite–rich grain boundary in the plagioclase rim.

Fig. 3: The unconventional barometry of Tajčmanová et al. (2014) applied to a plagioclase rim from Fig. 1a. See text for more details. The basis of the barometer is that pressure is solved so that the chemical potential difference $\mu_{Ab} - \mu_{An}$ has no spatial variation across the microstructure (see Tajčmanová et al., 2014 for details of the method). The calculations were performed assuming that temperature is 720°C.

Fig. 4: (a) Isochemical phase–diagram section calculated for the Na$_2$O–CaO–FeO–MgO–Al$_2$O$_3$–SiO$_2$–H$_2$O (NCFMASH) model system using the chemical composition of a pseudomorph after kyanite. The calculation was performed by Gibbs free energy minimization (Connolly, 2009) using the thermodynamic database of Holland & Powell (1998; revised 2003). The melt solution model was taken from White et al. (2007), spinel, sapphirine, garnet, cordierite from Holland & Powell (1998), amphibole from Wei & Powell (2003) and White et al. (2003), omphacitic clinopyroxene from Green et al. (2007), white mica from Coggon & Holland (2002), the ternary feldspar model from Fuhrman & Lindsley (1988) and chlorite from Holland et al. (1998). Note that the melt model is calibrated for metapelitic compositions and it is used to provide a qualitative constraint. Phase relations within the melt field should be treated with caution. The chemical composition of the pseudomorph is (in wt.%) Na$_2$O: 5.12, CaO: 5.68, FeO: 3.30, MgO: 2.09, Al$_2$O$_3$: 41.85, SiO$_2$: 41.96 and was estimated by modal analysis. (b) The anorthite content of plagioclase as a function of pressure for a constant temperature of 720°C.

Fig. 5: (a) Schematic figure showing the morphological characteristics of cusps-shaped concentration distributions developed by grain boundary diffusion. Note the curvature of the compositional isopleths. The grain boundary is represented by a finite–thickness zone of higher diffusivity. (b) Calculation example of the diffusion of a component $C$ adjacent to a grain boundary following the approach of Fisher (1951). The diffusion coefficient for the intragranular region is taken as unity and the diffusion coefficient of the grain boundary is equal to 100 ($D_{GB}/D_V = 100$). The diffusion coefficients are isotropic and constant. The effective grain boundary has a width equal to $Lx/300$, where $Lx$ is the length of the model in the $x$ direction ($\delta = 0.003$). The composition at the left boundary ($x=0$) is kept constant. The lowermost boundary ($y=0.5$) corresponds to the grain boundary and its composition evolves according to Eq. 1. Note that only the left half of the model is shown. (c) Calculation example of the diffusion of a component $C$ adjacent to a grain boundary following the approach described here. All parameters and boundary conditions as in (b). Note that only part of the model is shown ($0 \leq x \leq 0.5$, $0.5 \leq y \leq 1$).

Fig. 6: Numerical results for diffusion modelling in plagioclase considering a grain boundary. Pressure and temperature are set constant during diffusion (0.5GPa, 720°C). Diffusion coefficient ($D = 10^{-21}$) was chosen to be close to the real value (Yund, 1986). The initial composition of plagioclase is zoned. Concentration of plagioclase after a time period of ca 0.39ka (a) and a time period of ca 0.83ka (b). The left–boundary condition is a Dirichlet (constant composition) boundary condition. (c) and (d) are the
same as in (a) and (b) but for a Neumann (no flux) left–boundary condition.

**Fig. 7:** Schematic diagram showing that a potential source of plagioclase could be the consumption of the previous plagioclase and kyanite to produce plagioclase ± spinel ± corundum ± sapphire symplectites. Note that in the shaded part, the volume amount of plagioclase is 50% the initial one as estimated by modal analysis.

**Fig. 8:** Numerical results for diffusion modelling in plagioclase considering a grain boundary with Neumann (no flux) boundary conditions. Parameters are taken as in Fig. 6. The white line represents a reaction front where plagioclase is consumed. The velocity is constant and approximately equal to 10mm Ma\(^{-1}\) (~3.17·10\(^{-16}\) m sec\(^{-1}\)). Concentration of plagioclase after a time period of ca 0.39ka (a) and a time period of ca 0.83ka (b). The initial composition of plagioclase is zoned. (c) and (d) are the same as in (a) and (b) but for an initially constant composition.
Figure 1
127x103mm (300 x 300 DPI)
Figure 2
183x397mm (300 x 300 DPI)
Figure 3
62x50mm (300 x 300 DPI)
Figure 4

83x36mm (300 x 300 DPI)
Figure 6
161x135mm (300 x 300 DPI)
Figure 7
41x24mm (300 x 300 DPI)
Figure 8
160x134mm (300 x 300 DPI)