

# High-pressure/low-temperature metamorphism and the dynamics of an accretionary wedge

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## SUMMARY

The preservation and exhumation of high-pressure rocks is an important observation in understanding the geodynamics of orogenic processes. A numerical tool is developed to estimate quantitatively the effect of the complex interplay between the mechanical and thermodynamical behaviour, and to assess under which conditions the preservation of metastable denser phases is possible. A finite difference numerical method is used to solve the continuity, Navier–Stokes and thermal equations for a Newtonian compressible fluid medium. In the model we take into account a typical forcing induced by a subduction process in a collisional environment according to a corner flow model. We follow the evolution of different phases in the crust including a pressure–temperature-dependent phase transition in the numerical code. Although eclogite is formed at depth when the phase diagram is only prescribed from thermodynamics, it cannot reach the surface. The kinetic effects of thermally activated diffusion and of the nucleation processes are taken into account in the modelling of the phase transition. Our simplified model does not explicitly take into account the presence of water. It assumes that the rate of phase transformation can be computed from a knowledge of pressure, temperature and phase content. The parameters of the kinetic equations are empirically chosen to reproduce qualitatively the typical pressure–temperature–time paths recorded in the Alpine belt. To obtain significant concentrations of high-pressure phases at the surface, different activation energies for the prograde and retrograde reactions are needed. This difference may be related to changes in the water content of the crust between its burial and its exhumation.

**Key words:** corner flow, exhumation, phase kinetics, phase transitions.

## INTRODUCTION

In many orogenic belts, high-pressure metamorphic rocks are observed. These rocks, particularly in the Alps, have undergone a high pressure/temperature ( $P/T$ ) trajectory (Fig. 1). The rapid exhumation of eclogite facies rocks has been explained by various processes which probably took place simultaneously. Either the crustal load which caused the high-pressure metamorphism has to be removed or the eclogitic rocks must be transported through the overburden (Platt 1993).

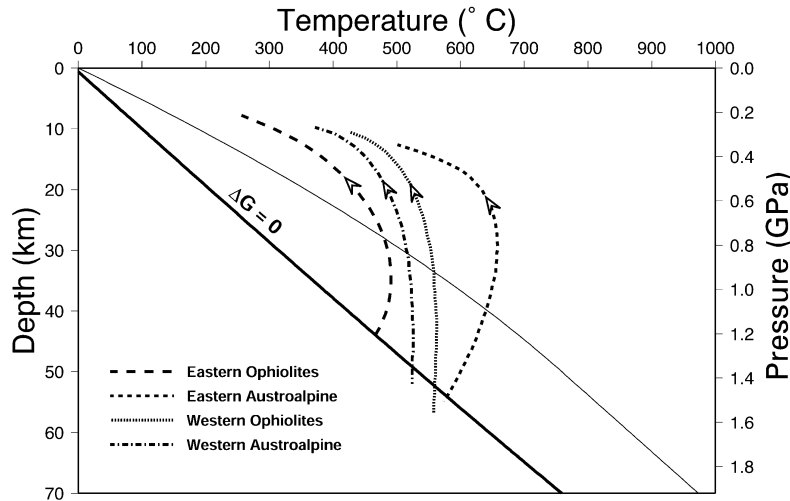
The removal of the crustal load may occur as a result of lithospheric extension, which takes place when the vertical stresses associated with the topography balance the regional compressive stresses (Froidevaux & Ricard 1987). Such a stress pattern is indeed observed in Tibet, the Andes, the Basin and

Range Province, and in other belts. This slow post-collisional process could be triggered and boosted by the delamination of the cold lithosphere (England & Houseman 1988) or even by the partial delamination of the dense gabbroic eclogites of the lower crust (Bousquet *et al.* 1997). The removal of the overburden is ultimately controlled by the erosion velocity.

The exhumation of high-pressure rocks can also be obtained through their intrusion in the cover owing to buoyancy forces. Such a process can either belong to continuum mechanics (diapirism) or invoke detachment faults (Chemenda *et al.* 1995) and the stacking of nappes (Gillet *et al.* 1986). The entrainment of small blocks is certainly possible. However, the fact that high-pressure crustal rocks may be denser than mantle rocks and are denser than low-pressure crustal rocks does not favour the upwelling of large metamorphosed bodies.

Corner flow models, where a subducting slab deforms an accretionary wedge limited by a hangingwall buttress, are also frequently invoked to explain the exhumation of high-pressure facies (Allemand & Lardeaux 1997). This results in a very rapid

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**Figure 1.** Typical  $P$ - $T$ - $t$  paths for high-pressure rocks in the Alpine belt from Spalla *et al.* (1996). The thin line is an average continental geotherm, and the thick line is the Clapeyron curve which limits the stability domains of the two phases.

upflow of material during the orogen at a velocity comparable to that of the subduction. In order to avoid stresses that are too great in the subducting plate, the average viscosity of the wedge should be quite low ( $\sim 10^{22}$  Pa s). This value seems unreasonable for lithospheric material, but comparable values are also required for fast upwelling of diapirs entraining high-pressure rocks through the wedge and for fast delamination of the lithosphere. We interpret this apparent low viscosity of the lithosphere as the equivalent viscosity of a material that may be weakened by the presence of faults, or in which the real viscosity may be stress-dependent or laterally variable.

It should be possible to discriminate among these various processes by comparing observations to model predictions. However, a useful model should not only solve the thermo-mechanical problem of simulating mountain building, but should also account for the thermodynamics and moreover the kinetics of phase transition. Modelling the kinetics is indeed a prerequisite because otherwise no high-pressure metamorphism at all would be observed at the surface. A precise computation of the large density changes associated with eclogitization is also necessary to test whether or not dense phases can be carried to the surface as entrained material.

In this paper we attempt to model the coupled problems of phase transformation and thermomechanical evolution in the framework of a corner flow scenario. As already noted, this process alone cannot explain all the complexities of the observations. We believe that the basic physics of the interplay between mineralogy and dynamics can be elucidated by this simple model, which could be made more complex and more realistic in future studies.

## PHASE KINETICS

Although the phase changes of crustal material towards high-density facies are complex (see Bousquet *et al.* 1997 for a review), we assume in this paper that they can be summarized by the following simple univariant phase change:

albite  $\rightleftharpoons$  jadeite + quartz.

Thus, the mineralogy of the crustal material is characterized by a variable  $\phi$  evolving from 0 (pure albite) to 1 (jadeite + quartz). This evolution is controlled by the following kinetic equation:

$$\frac{\partial \phi}{\partial t} + \mathbf{V} \cdot \nabla \phi = \Theta(P, T, \phi, t \dots), \quad (1)$$

where  $\mathbf{V} = (u, v)$  is the advection velocity. The reaction rate  $\Theta$  (in  $\text{s}^{-1}$ ) is obviously a function of pressure  $P$  and temperature  $T$ , which control the thermodynamic energy of the phases. Temperature is also an important parameter controlling the reaction kinetics, which depend on the phase content, the grain size and the fluid content of the transforming material and on the whole metamorphic path in the pressure-temperature-time ( $P$ - $T$ - $t$ ) space.

The sign of  $\Theta$  is given by the Gibbs free energy variation  $\Delta G(P, T)$  of the chemical equilibrium. This energy can be computed because the enthalpies, entropies, heat capacities and molar volumes of albite, jadeite and quartz are known as a function of temperature and pressure (Putnis 1992). The thermodynamic problem is therefore simple, but the modelling of the kinetics deserves more attention.

When two phases are in contact, the interface growth  $\Theta_1$  (in  $\text{m s}^{-1}$ ) is usually described by an Arrhenius equation,

$$\Theta_1 \sim T \text{sign}(-\Delta G) e^{-E/RT} (1 - e^{-|\Delta G|/RT}), \quad (2)$$

where  $E$  is an activation energy and  $R$  the gas constant. The activation energy can be a function of both  $P$  and  $T$  and can have different values in the prograde and retrograde directions. The reaction rate  $\Theta$  is related to this interface growth,  $\Theta_1$ , and also to the processes of nucleation. Experimentally, at given  $P$  and  $T$  conditions corresponding to a negative Gibbs free energy, a pure phase evolves towards a new phase following the so-called Avrami (1941) equation:

$$\phi = 1 - e^{-\beta(P,T)t^n}. \quad (3)$$

In this equation, the exponent  $n$  is a positive number and the coefficient  $\beta$  is related to the interface velocity and the nucleation rate  $\dot{N}$  (Burke 1965):

$$\beta \sim \dot{N} \Theta_1^{n-1}. \quad (4)$$

The proportionality factor can be estimated theoretically and depends on various assumptions for  $\dot{N}$  and  $n$ . The meaning of eq. (3) is simple. When  $n$  is large (typically 3–4), the sigmoidal evolution of the phase content through time indicates that the rate of transformation is not constant as would be implied by (2), but decreases to zero at the beginning and at the end of the reaction: at the beginning, not enough nuclei of the new phase are present; at the end, the impingement of grains of the new phase slows down the interface growth. When  $n$  is 1 or less, the growth rate is faster at the beginning when diffusion through the new phase is easy. As the diffusion distance further increases, the reaction rate decreases.

In the case of non-isothermal and non-isobaric transformations, the coefficient  $\beta$  is given by a cumbersome integral over the  $P$ – $T$ – $t$  path of the transformation (Rubie & Ross 1994; Kirby *et al.* 1996). Computing this integral is the only correct way to proceed. However, taking into account the various uncertainties or even ignorance of the relationships between activation energy or nucleation rates and pressure and temperature, we have decided to simplify the problem. We assume that the nucleation rate has a  $P$ – $T$  dependence of the same form as the interface velocity ( $\dot{N} \sim \Theta_1$ ). This may look like a drastic approximation, but the physics of both nucleation rate and crystal growth are closely connected: the two processes share the same activation energy, stop at thermodynamic equilibrium, and increase with the distance to equilibrium (Rubie & Ross 1994). Therefore, we write

$$\phi = 1 - e^{-(a\Theta_1 t)^n}, \quad (5)$$

where  $a$  is a constant. Eq. (5) indicates that 50 per cent of the initial phase is transformed in a time  $t_{1/2}$  given by

$$t_{1/2} = \frac{(\log 2)^{1/n}}{a\Theta_1}. \quad (6)$$

As one can assume that the reaction is either interface controlled or diffusion controlled, we consider the two cases  $n=4$  and  $n=1$ . In the first case, the behaviour of eq. (5) can be closely reproduced by solving the kinetic equation (1) with a reaction rate  $\Theta$  so that

$$\Theta = 4a\Theta_1[(\phi(1-\phi))^{3/4} + \epsilon], \quad (7)$$

where  $\epsilon$  is a small number needed for the reaction to start when  $\phi$  is 0 or 1. In order to obtain the same  $t_{1/2}$  time resulting from (5) by integration of (1) with (7),  $\epsilon$  has to be chosen as the implicit solution of

$$\int_0^{1/2} \frac{d\phi}{4[(\phi(1-\phi))^{3/4} + \epsilon]} = a\Theta_1 t_{1/2} = (\log 2)^{1/4}. \quad (8)$$

Numerically, eq. (8) leads to  $\epsilon = 10^{-3}$ . When  $n=1$ , eq. (7) is simply replaced by

$$\Theta = a\Theta_1(1-\phi) \quad \text{for the prograde reaction,} \quad (9)$$

$$\Theta = a\Theta_1\phi \quad \text{for the retrograde reaction.} \quad (10)$$

To apply the kinetic equations the values of the activation energies ( $E$ ) and prefactors ( $a$ ) are needed, but they have not been experimentally observed. The activation energies must be comparable to those of diffusional processes, which, for solid-state reactions, are of the order of 100–400 kJ. We can try to constrain the values of the prefactors from  $P$ – $T$ – $t$  path observations. Fig. 1 depicts typical retrograde paths for the Alpine belt (dashed lines). Also plotted are an average continental

geotherm (thin line) and the stability limit of the albite/jadeite phase change (thick line). For the continental geotherm we use a constant radioactive heat production  $Q$  of  $0.5 \mu\text{W m}^{-3}$  in the first 60 km with a constant heat flux of  $30 \text{ mW m}^{-2}$  at the base (the thermal diffusivity,  $\kappa$ , heat capacity,  $C_p$ , and density,  $\rho$ , are given in Table 1).

It is obvious that the crust does not cross the eclogite facies region under normal conditions. The burial of crustal rocks along a very cold geotherm is necessary in order to reach the jadeite stability field. Another striking feature of the observed  $P$ – $T$ – $t$  path is that decompression takes place at a rather constant temperature. In some cases (eastern Alps) the highest temperatures are reached during decompression in the albite stability field.

If we compute the phase content using eq. (7) with the same prograde and retrograde activation energies and prefactors we will face the following dilemma. If the velocity of prograde transformation is too low, no high-pressure metamorphism will occur. Even in the case where jadeite is formed during burial, the retrograde reaction will not allow the preservation of the metastable facies as the reverse transformation will be as fast or even faster because the exhumation takes place at a temperature that is greater than or equal to that of burial. The only possibility seems to be having a lower transformation rate for the retrograde than for the prograde direction at a given temperature. Such behaviour may be due to the work needed against pressure forces to expand the volume during retrograde metamorphism. This is indeed observed for two reactions that are well documented: the coesite–stishovite (Zhang *et al.* 1996) and calcite–aragonite transitions (Sotin & Madon 1988). Another possibility is that the increase in activation energy needed in our model for the retrograde reaction simply represents a decrease in water content of the crust during its exhumation.

From Fig. 1 it is seen that at 60 km depth and 450 °C the prograde reaction should occur, and that at 30 km and 650 °C the retrograde reaction should not occur. Therefore, we choose an energy activation and prefactor such that we obtain a half reaction time (see eq. 6) of 6 Myr for the prograde reaction (at 60 km depth and 450 °C) and 60 Myr for the retrograde reaction (at 30 km depth and 650 °C). Activation energies of 150 and 220 kJ for the prograde and retrograde reactions, respectively, and prefactors of the order of  $6 \times 10^{-5} \log 2^{1/n} \text{ s}^{-1}$  fulfil this requirement ( $10^{-6} \text{ s}^{-1}$  for  $n=4$ ). Of course, this choice is not unique as there is a perfect trade-off between energy and prefactor.

**Table 1.** Parameters of the corner flow model.

Symbol	Name	Value
$\alpha$	thermal expansion	$3 \times 10^{-5} \text{ K}^{-1}$
$C_p$	specific heat	$1 \text{ kJ kg}^{-1} \text{ K}^{-1}$
$\Delta T$	temperature gradient	$980^\circ$
$\eta$	viscosity	$10^{22} \text{ Pa s}$
$g_0$	gravity acceleration	$10 \text{ m s}^{-2}$
$H$	length scale	$10^5 \text{ m}$
$\kappa$	thermal diffusivity	$10^{-6} \text{ m}^2 \text{ s}^{-1}$
$\rho_c$	crust density	$2.8 \times 10^3 \text{ kg m}^{-3}$
$\rho_e$	eclogite density	$3.2 \times 10^3 \text{ kg m}^{-3}$
$dP/dT$	Clapeyron slope	$2.63 \text{ MPa K}^{-1}$
$Q$	heat production	$0.5 \mu\text{W m}^{-3}$

For this choice of parameters, Fig. 2 depicts the time of half reaction  $t_{1/2}$  given by equations (6) and (2) as a function of depth and temperature. This time of reaction is independent of  $n$ . The other thermodynamic data are taken from Putnis (1992). An average crustal density of  $2.8 \text{ kg m}^{-3}$  has been used to estimate the pressure-depth relationship.

Fig. 2 indicates that the reaction stops either when thermodynamic equilibrium is reached (roughly along the first diagonal) or when the temperature is too low to activate the reaction. In these two situations the time of half reaction is infinite. The reaction is the fastest in the two domains when  $t_{1/2}$  is minimum. As required by observations, the prograde transformation albite  $\Rightarrow$  jadeite + quartz is faster than the retrograde transformation (jadeite + quartz  $\Rightarrow$  albite) at a given temperature.

It is clear that our kinetic modelling only tries to mimic in a heuristic and macroscopic way the real complexity of the phase transition. In this paper, the reaction rate is ultimately controlled by two parameters only. The first,  $t_{1/2}$ , is the time needed for the transformation of 50 per cent of a pure phase at a single point of the  $P$ - $T$  space where this phase is metastable. Its choice controls the kinetic feasibility of the transformation. The second parameter,  $n$ , has a much smaller influence. It indicates whether the reaction is inhibited or accelerated by the presence of the new phase. From these two parameters the model predicts a reaction rate at every temperature, pressure and phase content. The fact that the microscopic mechanisms are certainly much more complex, with various possible paths for atom diffusion, with changes in grain size, etc., is beyond the scope of this paper. However, we believe that the macroscopic physics of phase transition kinetics is well represented by our approach. In the following, we only show results obtained with a value  $n=4$ . Other values have been tested but they are not shown because they lead to very similar results.

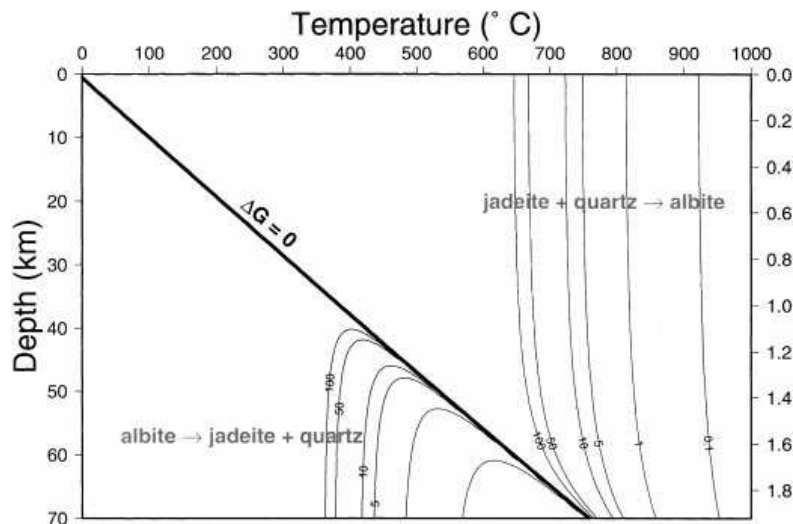
In this paper we consider that the laws of kinetics are not explicitly perturbed by fluids. It is known that water is a very efficient catalyst for the transformations (e.g. Rubie & Ross 1994; Wayte *et al.* 1989). As an example, at  $200^\circ\text{C}$  the

aragonite  $\Rightarrow$  calcite reaction is  $10^{12}$  times faster under wet than under dry conditions, although the two rates are comparable at temperatures in excess of  $400^\circ\text{C}$  (Rubie 1986). In the framework of our modelling, the presence of water may influence our results in two different ways. If the water is uniformly distributed, its catalyst behaviour is simply taken into account by a shorter time of half-transformation,  $t_{1/2}$ . The empirical parameters that we have used in our model and that are needed for eclogitized rocks to reach the surface implicitly take into account the necessary water content. The fact that we must increase the time of half-transformation during the exhumation may indicate that dehydration has occurred. If the water is localized into narrow cracks or layers of infiltration, the physics of the transformation overcomes the capabilities of our approach based on continuum mechanics. The fact that outcrops can be found in the field where almost unaltered jadeite is localized in proximity to jadeite that has completely reacted to an albite-rich assemblage shows that infiltration has occurred but it has not totally affected the retrograde metamorphism.

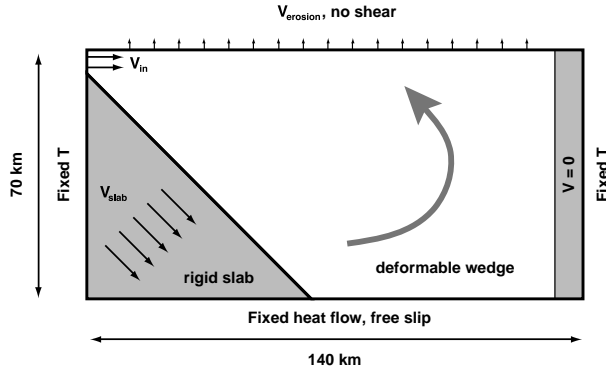
### THE THERMOMECHANICAL MODEL

An idealization of corner flow induced by a subducting plate is depicted in Fig. 3. The domain where the numerical modelling is performed is a 2-D box 70 km deep by 140 km wide. In the bottom left corner a uniform velocity field  $V_{\text{slab}}$  of a rigid plate dipping with an angle of  $45^\circ$  is imposed. On the right of the box the velocity is zero at the contact with the hangingwall buttress. At the two lateral borders the temperature has the imposed profile depicted in Fig. 1 (thin line). A free-slip condition is prescribed at the base of the box. At the surface, the shear stress is zero and a vertical component of the velocity simulates erosion and balances the flow entering at the top left of the box (displayed as  $V_{\text{in}}$  in Fig. 3).

In this domain the classic equations of fluid dynamics are applied. The deformable material of the wedge is considered to be characterized by a constant Newtonian viscosity. The



**Figure 2.** Transformation isochrons for the albite  $\Leftrightarrow$  jadeite + quartz reaction computed from eq. (6). The time required to reach 50 per cent transformation is contoured at intervals of 0.1, 1, 5, 10, 50 and 100 Myr. The thick line is the Clapeyron curve of the phase transition between albite and jadeite + quartz.



**Figure 3.** Geometry and boundary conditions of the corner flow model. The flow in the deformable wedge is induced by a fixed velocity field  $V_{\text{slab}}$  at the right corner. The fixed temperature profile on both lateral boundaries is the geotherm shown in Fig. 1 (thin line).

Navier–Stokes equation, in which the inertia terms are neglected (high Prandtl number approximation), reduces to

$$\eta \nabla^2 \mathbf{V} + \nabla P - \rho g_0 \hat{\mathbf{y}} = 0, \quad (11)$$

where  $\eta$  is the viscosity and  $g_0$  the gravity (see Table 1 for numerical values). In the wedge, the density can change due to eclogitization. In case of density changes another term should appear in (11), proportional to  $\eta \nabla(\nabla \cdot \mathbf{V})$ . This term has been lumped into the pressure gradient term. We are aware that using a viscous behaviour is clearly an oversimplification, but our goal is to describe the interplay between phase changes and dynamics rather than to provide a detailed analysis of the deformation pattern.

The density is a function of both phase and temperature and is given by

$$\rho = \rho_c + \Delta \rho \phi + \alpha \rho_c (T - T_0), \quad (12)$$

where we have assumed that the density changes due to temperature variations are identical for low- and high-density phases (same thermal expansivity  $\alpha$ ), and  $\Delta \rho = \rho_c - \rho_e$  is the density increase due to the phase transition. The mass conservation leads to the continuity equation in the anelastic approximation that takes the form

$$\nabla \cdot (\rho \mathbf{V}) = 0. \quad (13)$$

Finally, we consider the energy equation,

$$\kappa \nabla^2 T + \frac{Q}{\rho C_p} = \frac{\partial T}{\partial t} + \mathbf{V} \cdot \nabla T + \frac{L}{C_p} \Theta, \quad (14)$$

where  $L$  is the latent heat and  $\Theta$  the reaction rate (1) associated with the albite/jadeite phase transition. According to the Clapeyron relationship,  $L$  can be computed from the Clapeyron slope  $\gamma$  of the equilibrium  $P(T)$  line:

$$L = L(T) = T \frac{\Delta \rho}{\rho_c^2} \gamma \quad (15)$$

(see Table 1 for numerical values). It is important to consider exchanges of latent heat during metamorphic reactions as they slow down reaction progress (Ridley 1986). In the energy equation (14) the terms describing the frictional heating and the adiabatic compression are both neglected. The frictional heating would indeed have been overestimated as we do not use a temperature-dependent rheology which buffers this term.

Adiabatic heating has no effects over a thickness of 70 km. Heat can, in principle, also be efficiently carried by fluid transport. The depth range of our model, which is much larger than the depth at which permeability closes,  $\sim 10$  km (Brace 1980), makes this effect negligible also.

The differential equations (1), (11), (13) and (14) and eqs (7), (12) and (15) are solved simultaneously by a finite difference code implemented in a FORTRAN program. The 2-D finite difference solver for the Navier–Stokes and continuity equations, FDFLOW (Lemos 1994), has been modified to include the specifics of our problem. The domain is discretized by a staggered arrangement. The solution is obtained in two steps. In the first step, after the computation of temperature and phase, a temporary velocity field is calculated using (11); the resulting flow violates the continuity because it is computed using the pressure gradient at the old time level. In the second step, the continuity equation (13) is satisfied using an implicit pressure–velocity relaxation scheme (for details see Lemos 1994). The time integration is implicit for both  $\mathbf{V}$  and  $T$ . The addition of the energy equation to the original code has been benchmarked with published results (Blankenbach *et al.* 1989), obtaining very good agreements in the range of Rayleigh numbers where our code can be compared to these results.

## RESULTS

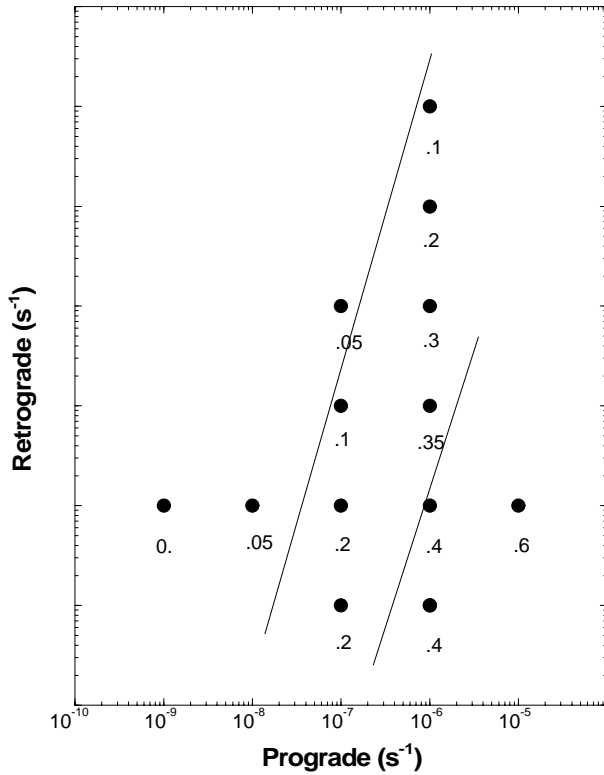
The previous equations have been written in their dimensional forms. However, the flow characteristics are controlled by a set of non-dimensional numbers. The most important are the Peclet number controlling the ratio of advected and conducted heat ( $Pe$ ) and a buoyancy number quantifying the ratio between internal and external imposed forces ( $R_\phi$ ):

$$Pe = \frac{V_{\text{slab}} H}{\kappa}; \quad R_\phi = \frac{\Delta \rho g_0 H^2}{\eta V_{\text{slab}}}. \quad (16)$$

In  $R_\phi$  only the bulk density change between normal and eclogitized crust is taken into account. Another ratio,  $R_T$ , scales the effect of temperature-induced density variations against external forces. This number is obtained by replacing  $\Delta \rho$  by  $\alpha \rho \Delta T$  in the definition of  $R_\phi$ , where  $\Delta T$  is the maximum temperature difference in the model. Clearly, because the density changes due to temperature variations are much smaller than those due to the phase change (12 per cent),  $R_T$  does not really affect the dynamics of the wedge.

$Pe$  is of the order of 20–200 (for  $H = 70$  km and  $V_{\text{slab}} = 1\text{--}10$  cm yr $^{-1}$ ). This means that heat is always advected rather than conducted. The viscosity of the wedge cannot be too high. Indeed, the stress field in the wedge is of the order of  $\eta V_{\text{slab}}/H$  and should not overcome a typical ridge push force, which is of the order of 100 bar. This results in the choice of a viscosity that does not exceed  $2 \times 10^{22}$  Pa s, which is more appropriate for the mantle than the lithosphere. This drawback is the consequence of the assumption of a linear (e.g. stress-independent) rheology. With such viscosities, the buoyancy number  $R_\phi$  has to be larger than 0.3. This shows that the flow, although dominated by external forces, is affected by internal loads.

In order to achieve high-pressure metamorphism a first requirement is of course to enter the jadeite stability field. With the chosen normal isotherm and a 45° dipping slab, the numerical simulations show that the subduction velocity must be larger than 0.3 cm yr $^{-1}$ . When eclogitization

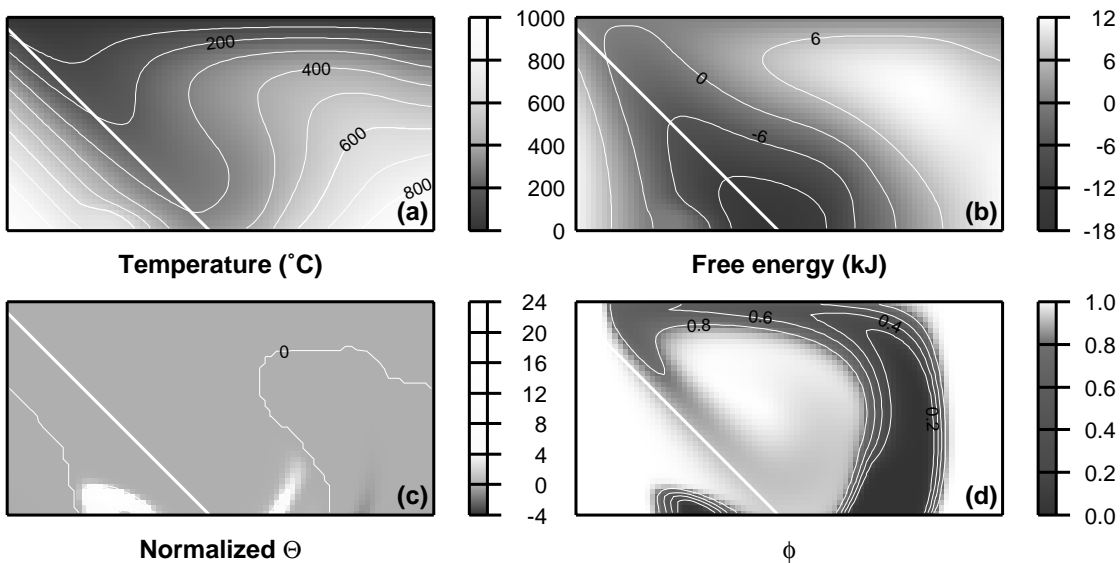


**Figure 4.** The percentage of jadeite+quartz at the surface is plotted as a function of the prefactors of eq. (7). The activation energies and the velocity of the slab are constant.

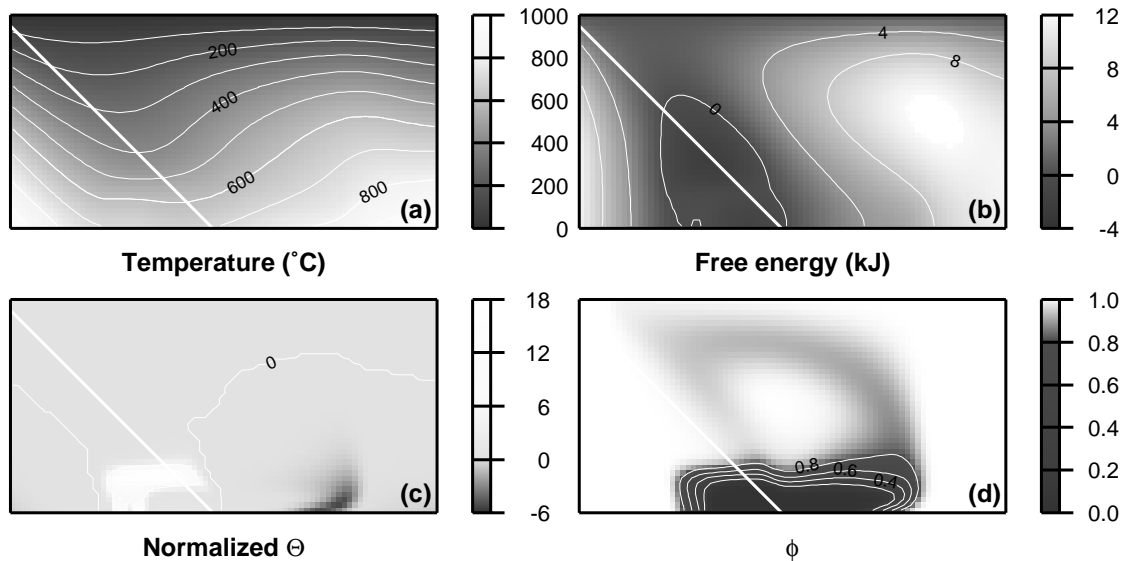
occurs, the dense crust can be brought up to the surface or re-transformed into the initial phase according to the choices of the prefactors in eq. (7). Fig. 4 shows the percentage of jadeite in the material reaching the surface as a function of

the prefactors for the prograde and retrograde reactions. A constant slab velocity of  $2 \text{ cm yr}^{-1}$  has been used and the duration of the experiment is 35 Myr, with the same activation energies used as in the computation showed in Fig. 2. For high values of the prograde prefactor, a significant percentage of jadeite+quartz is found at the surface, ranging from 5 to 50 per cent according to the retrograde prefactor. For low values of the prograde prefactor, the reaction takes too long when compared with the time spent by the crust under conditions of high-pressure metamorphism, and no jadeite is observed at the surface. Accordingly, for a given prograde prefactor, too high a retrograde prefactor prevents the conservation of dense phases during the upwelling. Because of the trade-off between prefactors and activation energies in eq. (7), a similar figure could be plotted fixing the values of the prefactors and allowing a variation in the activation energies for the prograde and retrograde reactions. Our model will benefit from new experimental values for the studied reactions when they become available.

Fig. 5 summarizes the behaviour of various quantities computed by the code. This simulation is performed with the kinetic prefactors equal to  $10^{-6} \text{ s}^{-1}$ , as used in Fig. 2. The other parameters given in Table 1 correspond to  $Pe=44$  and  $R_\phi=3$ . In Fig. 5(a), the temperature field is depicted through isolines  $100 \text{ }^\circ\text{C}$  apart. The surface of the slab is shown by a thick white line. The subduction advects the cold upper crust and takes it down to the stability field of jadeite. Fig. 5(b) represents the Gibbs free energy of the albite  $\Leftrightarrow$  jadeite + quartz reaction. Along the Benioff zone the stability area of jadeite corresponds to negative energy values. The most negative values are just at the surface of the slab. The area of highest thermodynamic stability for albite (positive  $\Delta G$ ) is around 30 km deep in the rear of the wedge. Because of the complex form of the phase kinetics equation, these areas of high energy do not correspond in any way to the area of fastest prograde or retrograde reactions (Fig. 5c). The fastest reaction rates are at the hottest borders of high-energy areas. The latent



**Figure 5.** (a) Temperature field, contoured in isolines of  $100 \text{ }^\circ\text{C}$ ; (b) Gibbs free energy in kJ; (c) normalized reaction rate  $\Theta$ ; (d) concentration of the albite mineral phase  $\phi$ . The model parameters are given in Table 1; the slab velocity is  $2 \text{ cm yr}^{-1}$ .



**Figure 6.** Same as Fig. 5 for a slab velocity of  $0.5 \text{ cm yr}^{-1}$  and a wedge viscosity of  $10^{21} \text{ Pa s}$ . (a) Temperature field contoured in isolines of  $100 \text{ }^\circ\text{C}$ ; (b) Gibbs free energy in kJ; (c) normalized reaction rate  $\Theta$ ; (d) concentration of the albite mineral phase  $\phi$ .

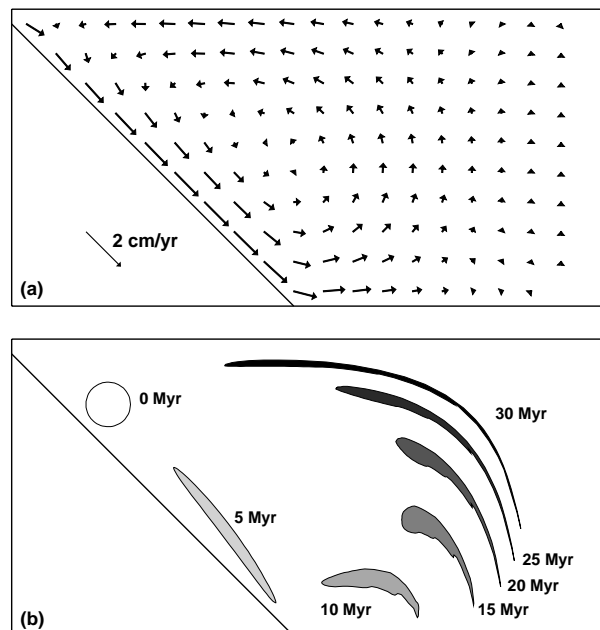
heat released by the prograde reaction reheats the slab, as shown in Fig. 5(a) (it is assumed arbitrarily that the subducted slab is composed of the same crustal material as the wedge). Between the fronts of prograde and retrograde reactions, the transformation rate goes to zero because the reaction has come to an end, even though the thermodynamics and thermal conditions should prescribe a fast rate. This is due to the  $\phi(1-\phi)$  term in eq. (7). Fig. 5(d) shows the percentage of low-pressure phase. The pattern is totally different from both that of the free energy and that of the reaction rate. In this example, the dense crust after exhumation is re-injected into the wedge.

With other kinetic prefactors, different shapes for the upwelling current of high-pressure rocks at depth can be obtained; raising the slab velocity tends to move the prograde reaction zone to the right, and increasing the velocity of the retrograde reaction decreases the percentage of high-pressure phase at the surface. However, as the surface velocity is quasi-horizontal and the phase content frozen by the low surface temperature, the model predicts a roughly uniform distribution of phases at the surface.

By decreasing both the slab velocity and the viscosity of the wedge, another kind of dynamics can be obtained. Shown in Fig. 6 are the results predicted for a slab velocity of  $0.5 \text{ cm yr}^{-1}$  and a viscosity of  $10^{21} \text{ Pa s}$ , which yield  $Pe = 11$  and  $R_\phi = 120$ . In this case, the isotherms are much less entrained by the subduction than in the previous case (Fig. 6a). However, this velocity is just large enough to cool down the crustal material into the jadeite stability field (Fig. 6b). The higher buoyancy number  $R_\phi$  forbids too rapid an ascent of the dense eclogitized phase, decreases the vertical velocity and thus gives the jadeite enough time to undergo a complete retrograde reaction. The eclogitized phase is therefore confined to a stagnant dense lid at the bottom of the box (Fig. 6d). This suggests that subduction has to be fast enough and the wedge stiff enough to bring high-pressure mineral phases to the surface, as in the Alps.

Until now, the results of the model have only been described from a Eulerian perspective. The very regular velocity pattern

that develops in the wedge, which is shown in Fig. 7(a), appears to be too simple to explain the complexity of the geology. However, the natural objects studied by geologists are the results of finite deformation akin to a Lagrangian description of the flow. In Fig. 7(b), the deformation through time of an initially spherical body illustrates the fact that even a simple flow with homogeneous linear viscosity induces complex finite deformation. This deformation closely resembles the nappe geometry commonly observed in collisional belts



**Figure 7.** (a) Velocity field in the wedge. (b) Finite deformation of an initially spherical shape advected by the flow. The parameters are the same as in Fig. 5.

(Polino *et al.* 1990). This suggests, as already stated in Allemand & Lardeaux (1997), that complex rheologies may not be necessary to model complex geological settings.

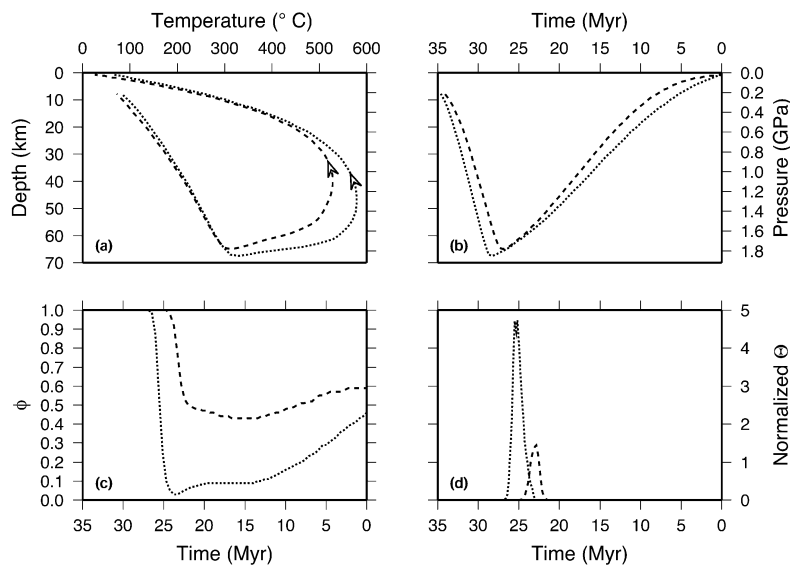
To illustrate differences in metamorphic records we consider two points reaching the surface at 30 and 70 km away from the trench. The corresponding trajectories and  $P$ - $T$ - $t$  paths have been computed by a Runge-Kutta method running backwards in time. The slab velocity is again  $2 \text{ cm yr}^{-1}$  and the subduction started 35 Myr before the exhumation of the particles. Fig. 8(a) shows their evolution in a  $P$ - $T$  diagram. In Figs 8(a) and (b), the pressure is given in gigapascals on the right vertical axis and the depth in kilometres is shown on the left axis; temperatures are in  $^{\circ}\text{C}$ . The particles undergo counter-clockwise motion, with the prograde path corresponding to the burial of upper crust on the left-hand side of Fig. 8(a). The burial takes place at a high velocity, which is of the order of the imposed slab velocity, and it takes 7–8 Myr to take the two particles from a depth of  $\sim 10 \text{ km}$  to  $\sim 65 \text{ km}$ . Shortly after reaching their maximum depths, the trajectories enter the high-transformation-rate field of the jadeite + quartz phase, and the phase transformation starts 27 and 25 Myr ago in Fig. 8(d) for the points emerging at 30 and 70 km, respectively. In Fig. 8(c) the fastest point, reaching a somewhat greater depth, is subjected to a higher grade of metamorphism, being almost totally transformed into the high-pressure phase; on the other hand, for the slower particle the transformation affects only 40 per cent of the material. Although the particles enter the region of high prograde transformation at only slightly different  $P$ - $T$  conditions, they enter the retrograde stability field with very different metamorphic facies. As shown in Fig. 2, at a depth of 60 km a difference in temperature of a few tens of degrees causes the reaction time to drop by a factor of 5 or more. This behaviour is related to the presence of the kinetic factor, which has an exponential dependence on the temperature.

The exhumation corresponds to the curved trajectories on the right-hand side of Fig. 8(a); such decompression takes more than 25 Myr to complete. The retrograde  $P$ - $T$  paths in Fig. 8(a) closely resemble the paths of some of the Alpine

units shown in Fig. 1. However, the  $P$ - $t$  trajectories (Fig. 8c) are different from those deduced by observation where the velocity of exhumation seems faster (Duchêne *et al.* 1997). A more refined model with a more realistic subduction history and geometry may allow us to make more quantitative comparisons with data. In this paper, we limit our attention to the physics of the phase transitions and to its relationship with the thermomechanical model.

## CONCLUSIONS

High-pressure facies rocks are widely studied because the mechanisms describing their formation and their subsequent exhumation are strongly linked to the dynamics of the orogeny itself. On the one hand they are investigated with respect to the thermodynamic properties of minerals, and on the other various mechanisms have been proposed in order to relate rock exhumation to various processes that may happen simultaneously or at different times during the formation of an orogen. In this work we have combined observations from mineral physics describing the metastability of the high-pressure facies and a simple mechanical model appropriate for any continental convergence zone. Despite the simplifying assumptions, the model is able to provide a synthesis of different observations and is able to relate various parameters, including the subduction rate, the phase kinetics rates and the viscosity of the crustal wedge, to the presence at the surface of the high-pressure phases. The predicted retrograde path shows a good qualitative agreement with observations in different Alpine domains. We predict that the convergence velocity must be greater than a threshold value of  $0.3 \text{ cm yr}^{-1}$  in order to reach the conditions of thermodynamically stable jadeite + quartz. In addition to the thermodynamics of the reaction, the effects of the kinetics owing to both grain growth and nucleation have been considered. The parameters that we use in the kinetic laws must be understood as phenomenological quantities that take into consideration an unknown fluid content. Clearly, they will have to be compared with



**Figure 8.** The dashed and dotted lines correspond to the trajectories of two points emerging at 30 and 70 km away from the trench, respectively. (a)  $P$ - $T$  path; (b)  $P$ - $t$  diagram; (c)  $\phi$ - $t$  diagram; (d)  $\Theta$ - $t$  diagram. In all these diagrams, 0 is present time. The parameters are the same as in Fig. 5.



laboratory experiments on kinetics in the future. This comparison will put constraints on the water content of the crust that has been buried and then exhumed. We have studied different distributions of the high-pressure phase at the surface after choosing a convergence velocity, mechanical parameters and a thermal regime. The different grades of metamorphism along the surface of the wedge (for rocks that experienced only slightly different  $P$ - $T$  peaks) are related to distinct variations with temperature and pressure of the reaction rate. With the geometry of our simulation, the fact that eclogites are denser than normal crust does not prevent their exhumation.

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#### REFERENCES

- Allemand, P. & Lardeaux, J.M., 1997. Strain partitioning and metamorphism in a deformable orogenic wedge: application to the Alpine Belt, *Tectonophysics*, **280**, 157–169.
- Avrami, M., 1941. Kinetics of phase change. III. Granulations, phase change, and microstructure, *J. Chem. Phys.*, **9**, 177–184.
- Blankenbach, B. *et al.*, 1989. A benchmark comparison for mantle convection codes, *Geophys. J. Int.*, **98**, 23–28.
- Bousquet, R., Goffé, B., Henry, P., Le Pichon, X. & Chopin, C., 1997. Kinematic, thermal, and petrological model of the Central Alps: Lepontine metamorphism in the upper crust and eclogitization of the lower crust, *Tectonophysics*, **273**, 105–127.
- Brace, W.F., 1980. Permeability of crystalline and argillaceous rocks, *Int. J. Rock Mech. Min. Sci. and Geomech. Abstr.*, **17**, 241–251.
- Burke, J., 1965. *The Kinetics of Phase Transformations in Metals*, Pergamon Press, New York.
- Chemenda, A.I., Mattauer, M., Malavieille, J. & Bokun, A.N., 1995. A mechanism for syn-collisional rock exhumation and associated normal faulting: results from physical modelling, *Earth planet. Sci. Lett.*, **95**, 225–232.
- Duchêne, S., Lardeaux, J.-M. & Albarède, F., 1997. Exhumation of eclogites: insights from depth-time path analysis, *Tectonophysics*, in press.
- England, P.C. & Houseman, G.A., 1988. The mechanics of the Tibetan plateau, *Phil. Trans. R. Soc. Lond. A*, **326**, 301–320.
- Froidevaux, C. & Ricard, Y., 1987. Tectonic evolution of high plateaus, *Tectonophysics*, **134**, 227–238.
- Gillet, P., Choukroune, P., Balleve, M. & Davy, P., 1986. Thickening history of the Western Alps, *Earth planet. Sci. Lett.*, **78**, 44–52.
- Kirby, S.H., Stein, S., Okal, E.A. & Rubie, D.C., 1996. Metastable mantle phase transformations and deep earthquakes in subducting oceanic lithosphere, *Rev. Geophys.*, **34**, 261–306.
- Lemos, C.M., 1994. FDFLOW: a FORTRAN-77 solver for 2-D incompressible fluid flow, *Comput. Geosci.*, **20**, 265–291.
- Platt, J.P., 1993. Exhumation of high-pressure rocks: a reviews of concepts and processes, *Terra Nova*, **5**, 119–133.
- Polino, R., Dal Piaz, G. & Gosso, G., 1990. Tectonic erosion at the Adria margin and accretionary processes for the Cretaceous orogeny of the Alps, *Mem. Soc. Geol. France*, **156**, 345–367.
- Putnis, A., 1992. *An Introduction to Mineral Sciences*, Cambridge University Press, Cambridge.
- Ridley, J., 1986. Modelling of the relations between reaction enthalpy and the buffering of reaction progress in metamorphism, *Mineral. Mag.*, **50**, 375–384.
- Rubie, D.C., 1986. The catalysis of mineral reactions by water and restrictions on the presence of aqueous fluid during metamorphism, *Mineral. Mag.*, **50**, 399–415.
- Rubie, D.C. & Ross, C.R., 1994. Kinetics of the olivine-spinel transformation in subducting lithosphere: experimental constraints and implications for deep slab processes, *Phys. Earth planet. Inter.*, **86**, 223–241.
- Sotin, C. & Madon, M., 1988. Generalized nonlinear inversion of kinetics data: application to the calcite  $\rightleftharpoons$  aragonite transformation, *Phys. Earth planet. Inter.*, **52**, 159–171.
- Spalla, M.I., Lardeaux, J.M. & Messiga, B., 1996. Tectonic significance of Alpine eclogites, *J. Geodyn.*, **21**, 257–285.
- Wayte, G.J., Worden, R.H., Rubie, D.C. & Droop, G.T.R., 1989. A TEM study of disequilibrium plagioclase breakdown at high pressure: the role of infiltrating fluid, *Contrib. Mineral. Petrol.*, **101**, 426–437.
- Zhang, J., Li, B., Utsumi, W. & Liebermann, R.C., 1996. In situ X-ray observation of the coesite-stishovite transition: reversed phase boundary and kinetics, *Phys. Chem. Miner.*, **23**, 1–10.