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Ethan F. Baxter · Donald J. DePaolo

Can metamorphic reactions proceed faster than bulk strain?

Abstract Available constraints on metamorphic reaction rates derived from the study of natural systems are similar to, or slightly lower than, the bulk strain rates measured in the same rocks. Here, we explore whether this apparent relationship is merely coincidence or due to a more fundamental mechanistic link between reaction and strain. Grain boundary migration accommodated dislocation creep (GBMDC) or grain boundary diffusion creep (GBDC) (i.e. pressure solution), both of which involve dissolution-precipitation as we define it, will occur simultaneously with mineral reactions involving dissolution-precipitation in the presence of a non-zero deviatoric stress. The exact relationships between reaction and strain are different depending on whether GBMDC or GBDC is controlling strain, but the mechanistic link exists in both cases. We present theoretical arguments which show that bulk strain by GBMDC or GBDC, which may additionally be accommodated by processes not involving dissolution-precipitation, such as dislocation glide and climb or grain boundary sliding, should in most cases be somewhat faster than the bulk reaction rates as observed. With few exceptions, for natural metamorphic systems undergoing plastic deformation, strain rates provide an upper limit for bulk reaction rates occurring simultaneously in the same rocks. The data suggest that mineral reaction rates may typically be within one order of magnitude of the strain rate.

E. F. Baxter (✉)
Division of Geological and Planetary Sciences,
California Institute of Technology,
Pasadena, California 91125, USA
E-mail: efb@bu.edu
Tel.: +1-617-3582844
Fax: +1-617-3533290

D. J. DePaolo
Department of Earth and Planetary Science,
University of California,
Berkeley 97420, USA

Present address: E. F. Baxter
Department of Earth Sciences,
Boston University, 685 Commonwealth Ave.,
Boston, Massachusetts 02215, USA

Introduction

As rocks are heated and stressed during metamorphism they may respond by changing mineralogy and compositions (chemical reactions) and by physically deforming (strain). It has been shown that chemical reaction and deformation processes may be linked in metamorphic environments (e.g. Brodie and Rutter 1985; Rubie and Thompson 1985; Snow and Yund 1987; Rutter and Brodie 1988, 1995; Yund and Tullis 1991; Graham et al. 1997, Skelton et al. 1997), fault zones(e.g. Rubie 1983; Knipe and Wintsch 1985; Stunitz 1998; Newman et al. 1999; Rutter 1999; Wibberly 1999; Steffen et al. 2001), and deep subduction zone earthquakes (e.g. Green and Burnley 1989; Kirby et al. 1991). For instance, deviatoric stress during deformation may provide energy or lead to mechanisms that enhance the progress of chemical reactions (Brodie and Rutter 1985; Knipe and Wintsch 1985; Snow and Yund 1987; Yund and Tullis 1991; Graham et al. 1997; Skelton et al. 1997; Stunitz and Tullis 2001), or the rate and occurrence of chemical reactions might influence the rate at which rocks can physically deform (Rubie 1983; Brodie and Rutter 1985; Rutter and Brodie 1988, 1995; Green and Burnley 1989; Kirby et al. 1991; Newman et al. 1999; Wibberly 1999;). Bulk reaction rates and strain rates, though measured in different ways, may be expressed in the same units (time^{-1}) and thus may be directly compared. Strain rate is often expressed as a change in length per unit length per unit time (length change/length/time), which may easily be understood in terms of the fractional volume or mass of rock that is involved in the strain. Reaction rate may similarly be

expressed as the fractional volume or mass of rock involved in reaction (mass reacted/mass/time). As reaction and strain may both involve the breakdown and reconstitution of mineral components, it could be hypothesized that the bulk reaction rate, R, would be related to, if not equal to, the bulk strain rate, $\dot{\epsilon}$. The relationship between reaction kinetics and strain rate for rocks experiencing metamorphism has remained obscure because, while measurements of natural strain rates exist, until recently there have been few ways to reconstruct the rates of metamorphic reactions in nature. Estimates of metamorphic reaction rates on the basis of extrapolations from laboratory hydrothermal experiments [which, despite the recognition that they probably overestimate natural reaction kinetics, have been relied upon heavily; see Baxter (2003) for discussion] have placed them many orders of magnitude higher than bulk strain rates measured in nature, which are 10^{-6} to 10^{-7} year^{-1} (or $\approx 10^{-14}$ s^{-1}; see Fig. 1 and references therein). This large discrepancy is difficult to believe if reaction and strain are linked at all. This paper reviews recent observations relevant to natural reaction and strain rates and on that basis presents a discussion of the possible mechanistic links and theoretically expected relative rates of reaction and strain in metamorphic systems undergoing plastic deformation.

Rates of metamorphic reactions in nature

In recent years, the rates or timescales of metamorphic reaction have been measured in nature by various approaches [see Baxter (2003) for a review]. The method introduced by Baxter and DePaolo (2000, 2002a) uses Sr isotopes to measure the rate of bulk solid dissolution and reprecipitation in an isotopically layered system. As the solid minerals dissolve and precipitate, Sr isotopes are passively exchanged between the bulk solid and the local fluid, or, intergranular transporting medium (ITM) (see below). The measured value is the fractional rate at which the Sr contained in the bulk solid is exchanged with the local ITM; hence the reaction rate is given in units of reciprocal time. The deduced rate is the gross rate of all the forward reactions occurring in the bulk rock, weighted for each mineral phase according to Sr concentration. Another method, described by Christensen et al. (1989, 1994) and by Vance and O'Nions (1992) measures the progress of a particular garnet-forming reaction by quantifying the time interval over which garnet porphyroblasts grow. The net rate of a garnet forming reaction relates to the dissolution (of reactant minerals)

Fig. 1 Comparison of reaction rate (*square*, *rectangles*) and strain rate (*dots*, *ovals*) data. *Dots/squares with error bars* represent data with reported errors, *ovals/rectangles* represent reported ranges. *Black symbols* indicate data derived directly from the field. Note that the field-based constraints on reaction rates are similar to estimates of strain rate. Previous predictions of natural reaction rates (*gray rectangle*), based on extrapolation of lab data, are many orders of magnitude too high. The laboratory-based prediction of reaction rates shown includes the full range of values calculated from the kinetic data and rate laws of Wood and Walther (1983), Helgeson et al. (1984) (pH-independent), Matthews (1985), Schramke et al. (1987) (using both the linear rate law of Lasaga and Rye 1993, and non-linear rate law of Lasaga 1986), and Heinrich et al. (1989) ($X_{CO2} = 0.1$). These calculations used $\Delta G = 5,600 \pm 3,400$ J, $T = 600$ °C, and reactive surface area of 20 cm^2/g, representative of the Simplon Pass field site. See Baxter and DePaolo (2002a, 2002b) for further details of these calculations
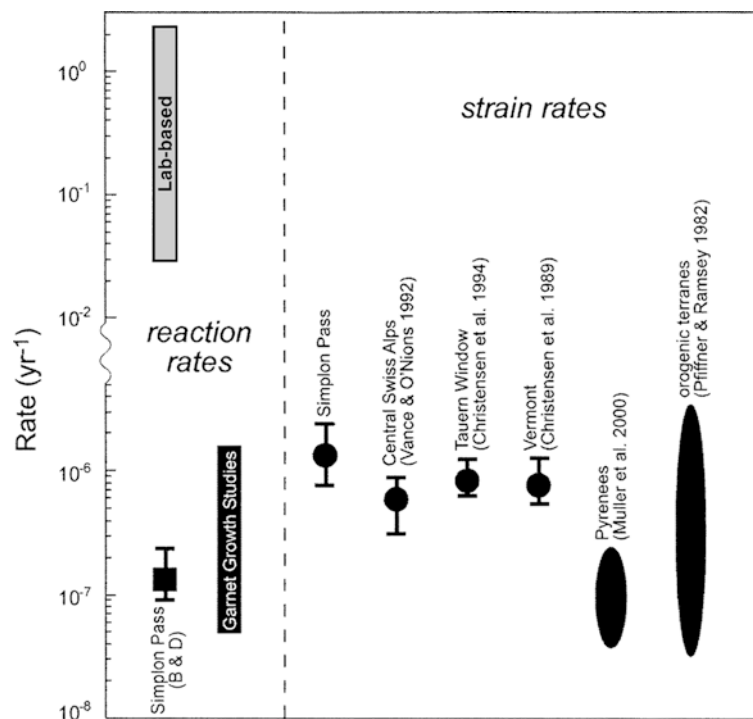
and precipitation (of garnet and other product minerals) in the rock [the net rate being the difference between the rates of the forward and backward reactions; see Lasaga (1986)] as well as limitations in the rate of intergranular transport of reactant and product species.

We employ the general term intergranular transporting medium (ITM) to refer to the fluid, melt and/or "dry" grain boundary network that, by definition, surrounds all mineral grains and through which all chemical transport and exchange between reacting minerals is facilitated. This is an important distinction, for as one typically thinks of "dissolution-precipitation" as involving a macroscopic fluid phase, we define the term "dissolution-precipitation reaction" more generally as any process involving (1) the breakdown of mineral components, (2) their introduction into the ITM (which may be dry!), (3) potential transport of mineral components within the ITM, and (4) subsequent reformation of the same or different minerals. Herein, unless otherwise stated, the term "bulk reaction" refers to the continuous dissolution, transport, and reprecipitation of mineral components in the bulk rock, as described in this paragraph. Bulk reaction rate, R, may be expressed in units of grams of solid reacted, per gram of bulk solid, per year ($year^{-1}$).

Bulk Sr exchange rates

Baxter and DePaolo (2000, 2002b) measured $^{87}Sr/^{86}Sr$ on whole rock and garnet mineral separates from both sides of an amphibolite–metapelite lithologic contact at a field site near Simplon Pass, Switzerland, that provided a large, premetamorphic contrast in the initial $^{87}Sr/^{86}Sr$ value. Whole rock data provide the final isotopic profile after the cessation of metamorphic exchange. Garnet data preserve a record of the isotopic profile in the ITM at the time of garnet growth, and thus provide a synmetamorphic initial condition from which modeling may proceed. The detailed shape of the final whole rock isotopic profile can be used in conjunction with numerical models of reactive transport to estimate the bulk Sr diffusivity in the rocks and the bulk Sr exchange rate, R. The exchange rate as measured by Baxter and DePaolo

(2000, 2002b) includes both mineral dissolution as well as solid-state diffusive isotopic exchange between the minerals and the ITM. Thus the reaction rate determined by the Baxter and DePaolo (2000, 2002b) method is strictly an upper limit on the bulk reaction rate, but mineral dissolution predominates over solid-state diffusion for most elements and hence the bulk reaction rate determined for Sr (or any other passive tracer) should be close to the bulk dissolution rate when the corrections are made for heterogeneous mineral Sr concentrations. The analysis at the Simplon Pass field site yields a Sr exchange rate $R = 1.4^{+1.1}_{-0.4} \times 10^{-7} yr^{-1}$, which is associated with metamorphic temperatures in the range 480–630 °C (Baxter and DePaolo 2000, 2002b). Baxter and DePaolo (2002b) argue that this rate is most indicative of the reaction rate of the dominant Sr-bearing phase, plagioclase, which constitutes about 20% of the rock volume and about 85% of the Sr. The reaction rate for the other phases (primarily amphibole) could be higher or lower, but is unlikely to have been too much different from the measured rate, considering that coupled reactions involving plagioclase and amphibole certainly operated in the rock.

Garnet growth rates

Isotopic measurements in large zoned garnet porphyroblasts have been used to date core and rim growth separately and thus retrieve a total garnet growth time interval. Table 1 shows the results of several studies that have employed this technique with a variety of isotope systems including Rb-Sr (Christensen et al. 1989, 1994), U-Pb (Vance and O'Nions 1992), and Sm-Nd (Vance and Harris 1999; Stowell et al. 2001; Baxter et al. 2002). Together these data provide garnet growth durations characterizing a variety of metamorphic settings ranging from 1.4–14.7 million years.

To extract a meaningful reaction rate from these data is not straightforward. While radial growth rates (in terms of millimeters of garnet per year) are easily obtained, they have little relation to the actual rate at which minerals in the bulk rock are dissolving and precipitating to form garnet. It is this rate that

Table 1 Data from garnet growth duration studies. *na* Data not available

Reference	Locale	Temperature[a] (°C)	Growth duration (my)	Strain rate ($year^{-1}$)	Reaction rate[b] ($year^{-1}$)
Christensen et al. (1989)	Vermont, USA	550–600[c]	10.5 ± 4.2	$7.6^{+5.0}_{-2.2} \times 10^{-7}$	$0.5–3.7 \times 10^{-7}$
Vance and O'Nions (1992)	Swiss Alps	480–530	2.9 ± 1.5	$6.0 \pm 2.8 \times 10^{-7}$	$1.6–16 \times 10^{-7}$
Christensen et al. (1994)	Tauern Window, Austria	455–475	5.4 ± 1.7	$8.5^{+3.8}_{-2.2} \times 10^{-7}$	$1.0–6.2 \times 10^{-7}$
Vance and Harris (1999)	Zanskar, Himalaya	570–700	~ 3.2	na	$2.2–7.2 \times 10^{-7}$
Stowell et al. (2001)	SE Alaska	590–735	≤ 5.5	na	$\geq 1.3–4.2 \times 10^{-7}$
Baxter et al. (2002)[d]	Scotland	500–660	8.1 ± 4.0	na	$0.6–5.6 \times 10^{-7}$

[a]Range of temperatures associated with garnet growth
[b]Fractional reaction rate calculated here assuming 50–90% reaction progress; see text
[c]Kohn and Valley (1994)
[d]Multiple stages of growth likely

determines how fast the net garnet forming reaction moves towards completion. To make a rough estimate of the reaction rate of the bulk rock associated with the garnet forming reaction, let us assume that the reaction has proceeded 50–90% to completion, a conservative range (see below). We can estimate the fractional reaction rate of the forward garnet forming reaction, R, in units of mass completely reacted/total mass/year with the following equation:

$$\frac{\%completion}{100} = 1 - \exp\left(-R \cdot \Delta t\right) \qquad (1)$$

where Δt is the duration of garnet growth. Results of these calculations, shown in Table 1, indicate that, for garnet growth durations of 1.4–14.7 million years, the corresponding fractional reaction rate is 0.5–16×10^{-7} year^{-1}.

The deduced rates of the garnet forming reactions have significant uncertainties. The uncertainty comes mainly from estimating the extent of reaction. We have used a range between 50 and 90%. Christensen et al. (1994) concluded that it was unlikely that the garnet forming reactions went to completion in their rocks. This conclusion follows from the observation that the time of termination of garnet growth was the same in two rock samples with differing bulk compositions. The same conclusions would seem to be favored by the observation that there was no slowing of garnet growth rate during the entire interval of growth, an observation that also applies to the Appalachian locality of Christensen et al. (1989). However, the possibility exists that the extent of reaction is less than 50%, which would have the effect of lowering the deduced reaction rate. However, since the modal amount of garnet in these rocks is close to 10%, and garnet modes in metapelitic rocks in general seldom exceed 20%, our lower limit of 50% reaction progress is probably reasonable.

Summary of natural constraints on reaction rates

Metamorphic reaction rates measured by either of the above methods yield values in the range 0.5–16×10^{-7} year^{-1}. These reaction rate estimates, particularly those derived from garnet growth studies, do have some complicating issues, but overall we believe that the derived values are representative of the bulk reaction rates that apply in nature and thus are useful for the purposes of this study. This range of values is many orders of magnitude lower than rates that have been inferred on the basis of extrapolations from laboratory data (Fig. 1). This large discrepancy likely results from fundamental differences between regional metamorphism and the cited lab experiments, perhaps most notably a disparity in free fluid content (greater in experiments, lesser in regional metamorphism) and resulting rate-limiting mechanisms (for example, see Thompson 1983; Rubie and Thompson 1985; Baxter and DePaolo 2002b; Baxter 2003). For the current purpose, it will suffice to say that the observations of *natural* regional metamorphic systems which we review here provide an opportunity to directly compare actual metamorphic reaction rates with metamorphic strain rates measured in the same rocks.

The approximate equality of the reaction rate measurement of Baxter and DePaolo (2000, 2002a, 2002b) and those estimated on the basis of garnet growth durations is noteworthy, and encouraging insofar as the reaction rates estimated from the garnet growth studies have significant uncertainty. The mineral growth studies record the progress of a net reaction, in the sense that net chemical reactions are usually thought to be the result of competing forward and backward reactions (that is, $R_{net} = R_f$–R_b; Lasaga 1986; Baxter and DePaolo 2002b). The Baxter and DePaolo (2000, 2002a, 2002b) study employs a method that directly measures the gross rate of all forward dissolution reactions (that is, R_f). As dictated by transition state theory (Lasaga 1986), the net rate of reaction (R_{net}) is strongly dependent on the departure from equilibrium, or chemical affinity for reaction, commonly denoted ΔG or A. Thus, one way to get very small net reaction rates is to have a very small departure from equilibrium. However, if ΔG is large, then $R_f >> R_b$ and R_{net} will be very similar to the gross forward reaction rate, R_f. Baxter and DePaolo (2002b) estimated the temperature overstep (and hence ΔG) at Simplon Pass to be large (~70 °C); hence the slow rates of reaction measured are unlikely to be a consequence of miniscule departures from equilibrium.

Syn-metamorphic strain rate estimates

Syn-metamorphic strain rates reported in the literature have been calculated from a variety of methods (e.g. Pfiffner and Ramsey 1982). Muller et al. (2000) dated syn-tectonic fibers in strain fringes using intergrown mineral pairs and Rb/Sr isochrons to determine time intervals and rates of deformation in a mylonitic shear zone. The technique of using rotated garnet porphyroblasts is the one we emphasize here(Christensen et al. 1989, 1994; Vance and O'Nions 1992) because strain rates can be estimated for the rocks where there is also information on reaction kinetics as noted above. Rotated garnets may simultaneously preserve a record of their total accumulated strain (in the form of sigmoid inclusion trails; Rosenfeld 1970) and the duration of their growth as discussed above. Garnet porphyroblasts in the amphibolite at the Baxter and DePaolo (2000, 2002b) field site at Simplon Pass exhibit rotated inclusion trails indicating syn-metamorphic deformation and present the possibility for strain rate estimation. From inclusion trails in a 6.5-mm-diameter garnet (Fig. 2), we estimate 1.4–1.6 radians of rotation during growth, which translates into 2.8–3.2 total simple shear strain (method of Christensen et al. 1989). Efforts to directly date these rotated garnets failed due to the adverse effects of mineral inclusions for precise determination of
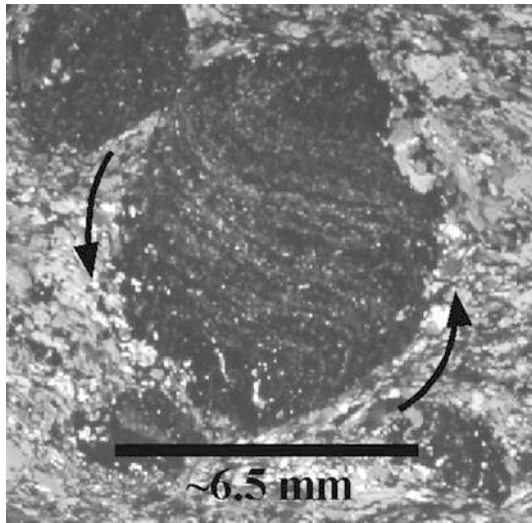
Fig. 2 Rotated garnet porphyroblast from the Simplon Pass field site. *Thin section photo* is taken in crossed polarized light. Lighter-colored sigmoid inclusion trails are visible within the large black garnet. [Figure reprinted, with permission, from Baxter and DePaolo (2002b)]

Fig. 3 Reaction rate vs. strain rate for the four localities where constraints on both exist: B&D (Baxter and DePaolo 2000, 2002b), C89 (Christensen et al. 1989), V&O (Vance and O'Nions 1992), and C94 (Christensen et al. 1994). Reaction rates in general are slightly lower than, but within an order of magnitude of, strain rates

either Sm/Nd or Rb/Sr ages (see Baxter and DePaolo 2002b). Using a conservative range of typical garnet growth rates measured by Christensen et al. (1989, 1994) and Vance and O'Nions (1992) (0.95–2.32 mm Ma^{-1}), we can estimate the total duration of garnet growth at Simplon Pass, $\Delta t = 3.4$–1.4 Ma, and thus a strain rate of 0.8×10^{-6}–2.3×10^{-6} year^{-1}. This agrees well with a strain rate estimate from nearby in the Central Alps (Vance and O'Nions 1992).

Observed relationship between reaction and strain rates

The deduced reaction rates for the four sites where there are appropriate data indicate that metamorphic reaction rates are typically smaller than, but within an order of magnitude of, the strain rates from the same site (Fig. 3). While relationships between the rates of reaction and strain have been discussed in the literature (see above), the data shown in Fig. 3 are the only quantitative indication of the actual relationships between the rates of metamorphic reaction and strain. We consider there to be two significant aspects of the data. One is that reaction rates are in general similar to strain rates, especially when compared with previous lab-based estimates of natural reaction rates which obscure this relationship (Fig. 1), and the other is that reaction rates are slightly smaller, by not much more than an order of magnitude, than the strain rates from the same rocks (Fig. 3).

In the following discussion we attempt to cast further light on the relationship between strain and metamorphic reactions. If reaction and strain rates are similar (as suggested by Fig. 1), then it is natur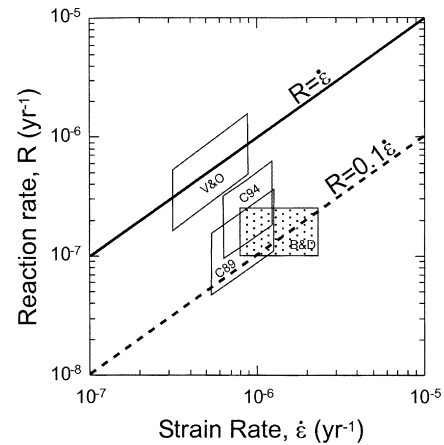al to ask if/how they might be linked mechanically. To begin the discussion it may be useful to ask under what conditions (if any) it is theoretically *possible* that reaction rates could be faster than strain rates. As we show below, it is impossible under most conditions for reaction rates to be faster than strain rates, because rocks may deform by either grain boundary migration accommodated dislocation creep (GBMDC) or grain boundary diffusion creep (GBDC) (i.e. pressure solution) at a rate equal to or exceeding the bulk dissolution-precipitation reaction rate if they are under non-hydrostatic stress as the mineral reactions are proceeding. Furthermore, it is clear that bulk strain can occur at rates faster than metamorphic reactions because there are additional strain accommodating mechanisms that are decoupled from chemical reaction mechanisms altogether. That is, when strain is accommodated by mechanisms other than GBDC or GBMDC it is because such mechanisms allow more efficient (i.e. faster) strain accommodation.

Why should reaction and strain rates be similar?

Bulk strain may be accommodated by a variety of mechanisms, some of which must involve 'bulk reaction' as we have defined it above, some of which do not. For our purposes, strain mechanisms may be divided into two groups on this basis (Table 2). Brittle mechanisms such as faulting or microcracking as well as cataclastic flow, grain boundary sliding, or slip along mineral cleavage planes do not require processing of material through the ITM and hence fall into what we call group 2 strain accommodation mechanisms. Bulk strain by group 2 mechanisms can be accomplished without any associated bulk reaction. Grain boundary diffusion creep (GBDC) (i.e. pressure-solution) and grain boundary migration accommodated dislocation creep (GBMDC) involve processing of material through the

Table 2 Categorization of strain mechanisms

Group #1 Strain mechanisms that involve reaction	Group #2 Strain mechanisms that do not involve reaction	
Grain boundary diffusion creep	Grain boundary sliding	Ductile regime
Pressure solution	Dislocation development and climb	
Coble creep	Subgrain development and rotation associated with dislocation creep	
Grain boundary migration accommodated dislocation creep		
	Cataclastic flow	Brittle regime
	Brittle fracture	

ITM, and hence fall into our designated group 1 strain accommodation mechanisms. GBDC and GBMDC are also believed to be the most important mechanisms for strain accommodation in crustal rocks under the conditions represented by the field sites in which both strain rate and reaction rate information exist.

Pressure-solution by definition is a reaction process involving dissolution of material at points of high stress and reprecipitation of mineral components after transport through the ITM to points of lower stress. The term "pressure-solution" usually connotes a low-temperature, fluid rich environment. The terms "grain boundary diffusion creep" or "Coble creep", essentially the same process, usually connote a higher-temperature, fluid-poor environment, and are often associated with finer grain sizes. While the effective rates of intergranular diffusion which may control the rates of these mechanism may vary as ITM characteristics vary (see, for example, Evans and Kohlstedt 1995), each of these processes (i.e. pressure-solution, Coble creep, GBDC) are essentially the same and may be modeled and described in a similar manner. Diffusion creep has been identified as an important strain mechanism in the mantle (Cooper and Kohlstedt 1984; Karato and Wu 1993) as well as in certain crustal environments (Handy 1989; Tullis and Yund 1991; Kruse and Stunitz 1999; Stockhert et al. 1999; Steffen et al. 2001; Wintsch and Yi 2002), in particular those characterized by small grain sizes.

Dislocation creep has been identified as the dominant strain mechanism for quartzofeldspathic rocks in typical crustal settings (Simpson 1985; Rutter and Brodie 1988; Yund and Tullis 1991; Hirth and Tullis 1992). Dislocation creep involves the development, migration, and consumption of dislocations within crystals under strain. While the internal development, glide, and climb of dislocations does not involve bulk reaction, dislocation creep strain also requires an accommodating mechanism for the removal of dislocations to prevent strain hardening and attain steady state creep (Poirier 1985; Hirth and Tullis 1992). Such dislocation creep "recovery" or accommodation mechanisms may include dislocation climb, subgrain development and rotation, and grain boundary migration (GBM). The first two of these do not involve bulk reaction, but GBM does. GBM is fundamentally a dissolution-precipitation phenomenon, whereby material on one side of the grain boundary is dissolved, its components transported through (and/or along) the ITM and new material precipitated on the other side of the grain boundary, thus facilitating its migration (Urai et al. 1986). In any rock where the mineral assemblage and/or the mineral compositions are not at equilibrium with respect to the pressure-temperature conditions and externally buffered chemical components, compositional changes (i.e. reaction progress toward the equilibrium condition) will accompany, or even enhance, GBM (Hay and Evans 1987; Yund and Tullis 1991; Stunitz 1998; Baxter and DePaolo 2002b). In this light, a mechanistic link between GBM accommodated dislocation creep strain and reaction has already been established.

At the Simplon Pass field site, plagioclase microchemistry exhibits patterns indicative of grain boundary migration as the primary means of exposing grain interiors to the ITM so that they can participate in chemical reactions (see Figs. 4 and 5 and Baxter and DePaolo 2002b). Steffen et al. (2001) have documented similar microchemical patterns in finer-grained rocks from the Greiner shear zone and interpreted them as evidence for grain boundary diffusion creep. Wintsch and Yi (2002) also describe mineral zoning patterns and truncations interpreted as dissolution-strain phenomena in an epidote-amphibolite grade gneiss in Connecticut. For the current purpose, the difference in interpretation of these microchemical patterns is not important, as all are clearly group 1 mechanisms involving reaction. The rocks at Simplon Pass also display a fabric of aligned amphiboles and biotites (Baxter and DePaolo 2002b) indicating that some group 2 strain processes (i.e. grain boundary sliding, and slip along biotite cleavage planes) also contributed to the bulk strain. Similar processes may also have contributed to strain in the Steffen et al. (2001) and Wintsch and Yi (2002) rocks.

In general, when strain is accommodated by either grain boundary diffusion creep (GBDC) or grain boundary migration accommodated dislocation creep (GBMDC), we expect a direct relationship between the rates of strain and reaction. Additional strain accommodated by group 2 strain mechanisms will serve to increase the total strain rate relative to reaction rates.

Equations relating reaction rate and strain rate

For the two group 1 strain accommodation mechanisms discussed above, it is possible to derive expressions relating the bulk rates of reaction and strain in a rock. The derived expressions focus on the *relative* rates of reaction and strain, rather than the driving forces and limiting factors that determine what the *absolute* rates will be. Below, we treat separately the relationship of reaction rate with GBDC and GBMDC strain.
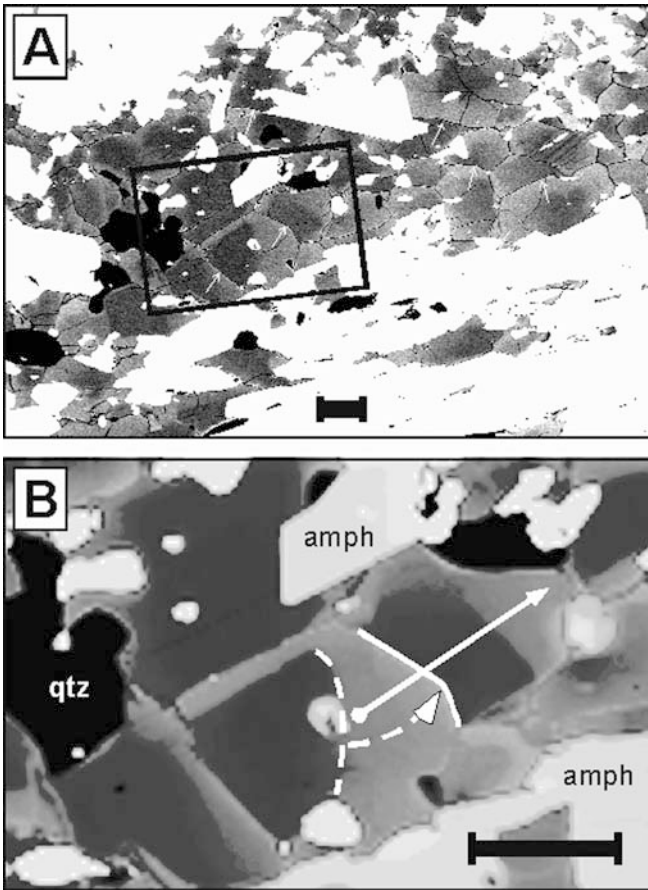
Fig. 4 Plagioclase in sample 97 BSP5-W, from the Simplon Pass field site, documenting grain boundary migration. **A** BSE image of plagioclase region. Note the compositional heterogeneity. *Small white arrows* show locations of sharp compositional gradients across grain boundaries. **B** Close-up calcium X-ray map of plagioclase grains. *Brighter color* indicates higher calcium. *White arrow* shows location of probe traverse (Fig. 5). The grain boundary has swept from its inferred past location (*dashed line*) to its current location (*solid line*) leaving in its wake a new, higher Ca plagioclase, and consuming older, lower Ca plagioclase. *Scale bars* of 100 μm are shown. [Figures reprinted, with permission, from Baxter and DePaolo (2002b)]

Grain boundary diffusion creep (GBDC)

Case 1: simple isochemical pressure solution effects in a mono-mineralic rock

The simplest case where the relationship between strain rate and reaction rate can be illustrated is for pressure solution in an isochemical, mono-mineralic system. Others have presented theoretical descriptions of pressure solution, including its relationship to reaction rates (e.g. Rutter 1983; Green 1984; Evans and Kohlstedt 1995; Lehner 1995; Paterson 1995; Shimizu 1995), but here we reproduce the conceptual model described by Turcotte and Schubert (1982) in condensed form and with some modification. The isochemical model is too simple to fully describe the complexities of most metamorphic rocks, but it can be used as a starting reference.
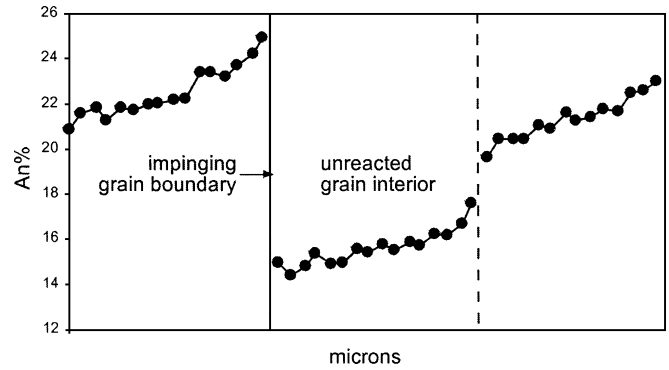

Fig. 5 Electron microprobe traverse of plagioclase grains as shown in Fig. 4B. *An%* stands for the percent anorthite end-member of plagioclase. Note the compositional asymmetry about the impinging grain boundary (*solid line*). *Dashed line* represents the inferred past location of another grain boundary which itself has migrated to the right of the view. [Figure reprinted, with permission, from Baxter and DePaolo (2002b)]

Consider a single mineral grain surrounded by a fluid ITM (Fig. 6). The mineral grain is cubic with side length "h". The grain boundary fluid has thickness "δ". The grain is held at ambient pressure P and temperature T (an oversimplification for now, but see below), and subject to a deviatoric compressive stress σ in the x direction, a deviatoric extensional stress of $-\sigma$ in the y direction, and no deviatoric stress in the z direction. The solubility of the mineral phase in the fluid is taken to be pressure dependent, solubility increasing with pressure. The equilibrium concentration of dissolved mineral components in the fluid at P and T is denoted c_{eq} (in moles per unit volume), and the pressure dependence is given by:
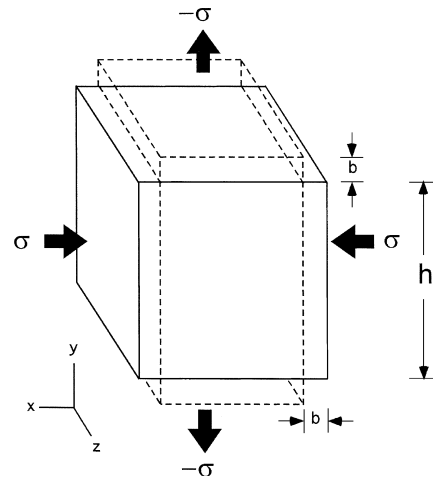

Fig. 6 Model for pressure solution effects. Deviatoric stresses σ and $-\sigma$ (in the x and y directions respectively) are applied to a cubic crystal of dimension h. Preferential dissolution occurs on sides normal to the x direction, and preferential crystal growth occurs on sides normal to the y direction. Reaction rate, R, is exactly equal to absolute value of strain rates. [Adapted from Turcotte and Schubert (1982)]

$$\left(\frac{\partial \ln c_{eq}}{\partial P}\right)_T = \frac{\Delta V_{sol}}{RT} \qquad (2)$$

where ΔV_{sol} is the partial molar volume change for the dissolution reaction. Hence the equilibrium solute concentration (c in moles/cm^3) in the fluid surrounding the sides normal to the x direction is higher than the value corresponding to the ambient pressure by:

$$c_x - c_{eq} = c_{eq}\left[1 - \exp\left(\frac{\Delta V_{sol}}{RT}\sigma\right)\right] \cong c_{eq}\frac{\Delta V_{sol}}{RT}\sigma \qquad (3)$$

The solute concentration in the fluid surrounding the side normal to the y direction is correspondingly lower. Since $RT/\Delta V_{sol}$ has the units of pressure, it can be denoted simply as σ_{sol}. Hence the equilibrium values of solute concentration on the sides normal to the x, y, and z direction are:

$$c_x = c_{eq} + c_{eq}\frac{\sigma}{\sigma_{sol}} \qquad (4a)$$

$$c_y = c_{eq} - c_{eq}\frac{\sigma}{\sigma_{sol}} \qquad (4b)$$

$$c_z = c_{eq} \qquad (4c)$$

The deviatoric stresses create chemical potential gradients in the grain boundary fluid, which in turn cause transport by diffusion through the fluid. The net transport is from the sides normal to the x direction to the sides normal to the y direction.

The rate at which this transport occurs depends on the dissolution rates and on the concentration gradients in the grain boundary fluid. The concentration gradient depends on the competition between dissolution and precipitation at the grain boundaries and diffusion within the fluid. If dissolution is slow relative to diffusion, the gradients are small and the fluid has a solute concentration that is close to c_{eq} on all sides. If dissolution is fast relative to diffusion, the solute concentrations are maintained at values approaching those dictated by Eqs. (4a, 4b and 4c). However, the net dissolution rate goes to zero as the equilibrium solute concentration is reached, so the system will be maintained at a steady state where the dissolution is balanced by the diffusive fluxes away from the dissolving crystal faces.

The timescale for diffusion is given by h^2/D. The time scale for dissolution, which is effectively the residence time of solute in the grain boundary ITM, is given by:

$$\tau_{diss} = \frac{\delta h^2 c_{eq}}{2h^2 R_s} = \frac{\delta c_{eq}}{2R_s} \qquad (5)$$

where R_s is the dissolution rate in moles cm^{-2} s^{-1}. The ratio of these two timescales is a Damkohler number:

$$N_D = \frac{\delta c_{eq}D}{2h^2 R_s} \qquad (6a)$$

The dissolution rate, R_s, can be expressed as the product of a far-from equilibrium rate (R_{so}) and the departure of the solute concentration from equilibrium (i.e. $\Delta G_r/\Re T$), which in this case of constant ambient P-T-X is simply σ/σ_{sol} (see Eqs. 4a, 4b and 4c). The equation therefore can be written as:

$$N_D = \frac{\delta c_{eq}D\Re T}{2h^2 R_{so}\Delta G_r} = \frac{\delta c_{eq}D\sigma_{sol}}{2h^2 R_{so}\sigma} \qquad (6b)$$

The pressure solution strain rate is transport-limited when this number is small, and dissolution rate-limited when this number is large.

If the rate of pressure solution is limited by the dissolution flux, we can express the flux from the x-normal sides as:

$$J_{diss} = \frac{2R_{so}\sigma h^2}{\sigma_{sol}} \qquad (7)$$

The reaction rate (and thus the strain rate) as we define it is this flux divided by the total number of moles of solid ($= h^3\rho_s/M$):

$$R = \frac{2R_{so}\sigma M}{h\rho_s\sigma_{sol}} = \frac{d\varepsilon_{xx}}{dt} = -\frac{d\varepsilon_{yy}}{dt} \quad \text{(dissolution limited case)} \qquad (8)$$

where M is the molecular mass of the solid.

If diffusive transport in the grain boundary fluid is rate-limiting, then it can be inferred that the solute concentration gradient between the dissolving and growing crystal faces will be close to:

$$\frac{dc}{d\zeta} = \frac{2\sigma c_{eq}}{\sigma_{sol}h} \qquad (9)$$

where ζ is a coordinate along the crystal surface. The reaction rate, given by the total diffusive flux away from the x sides, divided by the total mass of solid, is:

$$R = \frac{12\delta\rho_f D\sigma}{h^3\rho_s\sigma_{sol}} = \frac{d\varepsilon_{xx}}{dt}$$
$$= -\frac{d\varepsilon_{yy}}{dt} \quad \text{(grain} - \text{boundary diffusion limited case)} \qquad (10)$$

where ρ_f and ρ_s are the densities of fluid and solid respectively. In either the dissolution or diffusion limited case, this model leads directly to:

$$\frac{d\varepsilon_{xx}}{dt} = -\frac{d\varepsilon_{yy}}{dt} = R \qquad (11)$$

Furthermore, following Turcotte and Schubert (1982) it can be shown that

$$\mu_{ps} = \frac{\sigma}{2R} \qquad (12)$$

Equation (12) shows explicitly the relationship between stress, reaction rate, and the effective viscosity (μ_{ps}) of the rock material for this simple case. For stresses in the order of 10 MPa, the natural reaction (and strain) rate of $R = 3\times 10^{-7}$ year^{-1} ($\approx 10^{-14}$ s^{-1}) leads to a viscosity of

about 5×10^{20} Pa-s. For the same stress and a reaction rate of 3×10^{-2} year^{-1}, the viscosity is 5×10^{15} Pa-s. The latter viscosity value is exceptionally small for solids at temperatures of ca. 600 °C; typically cited estimates for mid-crustal ductile viscosity are in the range 10^{18}–10^{21} Pa-s (e.g. Kruse et al. 1991; McKenzie et al. 2000). Lower viscosities could be possible only for partially molten rocks (e.g. McKenzie et al. 2000). Put another way, the pressure solution model for reaction and strain implies that the measured strain rates of ca. 10^{-6} year^{-1} (see Fig. 1) are produced by deviatoric stresses in the order of 10–100 MPa; deviatoric stresses much greater than this are unlikely in the ductile mid-crust (e.g. Kruse et al. 1991). If one were to argue that the reaction rates were in fact much higher, such as 10^{-2} year^{-1}, to maintain reasonably high viscosity of $> 10^{18}$ Pa-s would require a deviatoric stress of less than 3,000 Pa, about the same order as atmospheric pressure variations. Based on these arguments, either it is obvious that reaction rates in the crust are not much higher than 10^{-6} year^{-1} (that is, similar to measured strain rates), or the pressure solution model does not apply in the more general incongruent multi-mineralic case.

Case 2: incongruent pressure solution in multi-mineralic rocks with changing P-T-X

The general model for regional metamorphism is that rocks are being subjected to changing pressure, temperature, and in some cases composition, with time. Hence, at all times the mineral assemblage is out of equilibrium and reactions among system phases tend to occur, altering the mineral assemblage and/or chemistry according to the P-T-X change. As reactions proceed, product minerals reflecting the change in mineral chemistry and/or assemblage will also have the tendency to recrystallize at the *locations* (i.e. crystal faces) of least stress. This process is frequently called incongruent pressure-solution. In the general case, we re-emphasize that, while the characteristics of the ITM may vary (fluid filled, dry, etc.), the equations we used to describe the general GBDC process apply identically, though some familiar terminology which connotes a fluid-filled ITM (such as "solute" and "aqueous") would need to be modified. Our discussion of the *relative* rates of GBDC strain and bulk reaction is *not* predicated on the characteristics of the ITM, and the same conclusions thus apply for wet and dry cases.

Specifying grain boundary solute fluxes for this case is much more complicated than for the single mineral case, but certain aspects of the model still apply. In general, the solubility of all minerals varies with pressure and hence there is always a tendency for solute fluxes to develop that will produce strain to accommodate a deviatoric stress. In general, for any reaction where $\Delta V_r < 0$, the reactants are more unstable where pressure is higher. Hence, in the situation analogous to that in the single mineral example (Fig. 6), the reactant minerals dissolve preferentially on the sides normal to the compressive deviatoric stress, and either grow, or dissolve more slowly, on the other sides (also see Wintsch and Yi 2002). This causes net solute fluxes that are analogous to those in the single mineral case, and generates strain in response to deviatoric stresses. The product minerals grow in preference to the reactant minerals, but will also have a tendency to preferentially grow in directions normal to the maximum compressive deviatoric stress because their solubility also increases with pressure.

The primary role of disequilibrium related to ambient P-T-X change should be to enhance dissolution rates of reactant minerals by enhancing the total free energy change in the dissolution reaction. Where pressure-solution is reaction rate limited, this will have an equal effect on the rates of strain and reaction (Eq. 8). Where pressure-solution is transport limited, this effect becomes a potential complicating issue, but may be negligible in most situations (see below).

Reaction vs. strain lengthscale for the transport limited process

In the general case, Eq. (10) does not apply because additional contributions to the local ΔG_{rxn} (i.e. changes in ambient P-T-X), which do not increase the chemical potential *difference* driving GBDC-related ITM-diffusion around grains, may allow bulk reaction to proceed at a rate independent of the GBDC strain rate. If diffusive transport in the ITM is rate-limiting for GBDC, then the remaining critical issue in comparing the rate of GBDC strain and bulk reaction is the diffusive lengthscale required to complete both the free-energy minimizing reaction and the free-energy minimizing reconfiguration (strain) of material. To illustrate this, consider a system comprising spherical grains of radius r. The reaction length, L_e, which compares the rate of reaction and intergranular transport, indicates the lengthscale over which reactants may freely participate in ongoing local reactions (see DePaolo and Getty 1996). If the reaction length L_e [$L_e = (D/RMK)^{1/2}$, where D is the molecular diffusivity of the slowest reactant species in the local ITM, R is the bulk reaction rate, M is the solid/ITM mass ratio, and K is the solid/ITM equilibrium partition coefficient (solubility) of the slowest diffusing species] is greater than the distance required for material to be transported from sites of high to low stress (roughly a distance of $\pi r/2$), then GBDC strain rate will not be inhibited by intergranular transport rate relative to the *bulk* reaction rate, and pressure solution strain may always proceed at (at least) the rate of ongoing bulk reaction. However, if L_e is smaller than $\pi r/2$ then local reaction (among phases within a distance L_e) may proceed faster than material has time to move to locations of lower stress, hence allowing reaction rate to exceed the rate of GBDC strain. It must be stressed that this outcome is only meaningful for reactions involving reactants located within a distance L_e of each

other—otherwise, the reaction will be similarly limited by the diffusive travel distance required for reactant species to come together.

This threshold (i.e. when $\pi r/2 = L_e$) may be quantified by considering natural bulk reaction rates and grain boundary diffusivities. Let us explore the limits of slow natural intergranular diffusivities by considering the case for Si (as the rate-limiting major species) diffusion in dry grain boundaries (i.e. no free fluid phase in the ITM). Using the surface area normalized regional metamorphic reaction rate, $\dot{R}$, of 10^{-9} g cm^{-2} year^{-1} (Baxter and DePaolo 2002b) and a reactive surface area of $r/3$ cm^2/cm^3 for spherical grains (e.g. Lasaga et al. 2000), we arrive at the following relation:

$$L_e = \left(\frac{D}{RMK}\right)^{1/2}$$
$$= \left(\frac{D(1/2 \cdot 3/r \cdot \delta)\rho_{ITM}}{K\bar{R}(3/r \cdot 1/\rho_s)\rho_s}\right)^{1/2} = \left(\frac{D\delta\rho_{ITM}}{2K\bar{R}}\right)^{1/2} \quad (13)$$

Thus, inserting the above value for $\dot{R}$, a value of $K=1$ (for Si in a "dry" grain boundary), $\rho_{ITM}=3$ (similar to solid mineral grains), and $D\delta=5.4\times10^{-12}$ cm^{-3} year^{-1} (for Si in anhydrous conditions at 600 °C; Farver and Yund 2000), we find $L_e=0.9$ mm. Thus, for these parameters, GBDC strain rates could be exceeded by *local* reaction rates only for grain radii greater than $2/\pi 0.9 = 0.6$ mm. Such average matrix grain sizes would be on the larger end of the spectrum for much of the crust, though likely more representative of deeper portions. More importantly though, as noted above, this outcome would only be meaningful for reactions where all participating reactants are located within the distance L_e, which would have to be minerals in grain to grain contact or at fortuitous triple junctions where several reactants meet closely. This would mean that "corona" type reactions between contacting minerals A and B to make mineral C could—in these conditions of slow ITM-diffusion controlled processes—proceed (initially) faster than strain. However, once a product corona layer develops between reactant phases at the grain boundary, the smaller product grain size, and/or slower volume diffusion limitation through the thickening product layer, would again result in reaction rates no greater than bulk strain. Also, volume changes associated with the corona reaction would produce some finite strain which, alone, could help prevent reaction rates from exceeding strain rates for very long.

Additional contribution to GBDC from grain boundary sliding

Poirier (1985) suggests that some amount of grain boundary sliding is inexorably linked to GBDC, as confirmed by experimental observations (Tullis and Yund 1991). So, for GBDC the bulk strain rate could be faster than the bulk reaction rate if grain boundary sliding adds a component of strain not already accounted for by the transport of material through grain boundaries to sites of reprecipitation. Therefore, based on the foregoing analysis, given a non-zero deviatoric stress, strain by GBDC will in most natural systems be able to proceed at least as fast as the bulk dissolution-precipitation reaction:

$$\dot{\varepsilon}_{GBDC} \geqslant R \quad (14)$$

That is not to say that GBDC will always be the *dominant* strain mechanism. However, if reaction is ongoing and there exists any non-zero deviatoric stress, then strain can and will proceed *at least* at the reaction rate by the GBDC mechanism. More efficient strain mechanisms can only lead to even faster strain rates relative to reaction rates, as in the case of GBMDC discussed next.

Grain boundary migration accommodated dislocation creep (GBMDC)

GBMDC may be a more efficient strain accommodating process than GBDC for much of the crust. The "Bailey–Orowan equation"(see Poirier 1985) shows that the steady state strain rate,$\dot{\varepsilon}$, may be expressed in terms of a recovery rate, r' (in units of stress/time), and a hardening coefficient, h' (in units of stress/strain), as:

$$\dot{\varepsilon} = \frac{r'}{h'} \quad (15)$$

For steady state GBMDC, internal stress remains equal to the applied stress during steady state creep as the rate of recovery (i.e. dislocation consumption) is balanced by strain hardening through the development of new dislocations within the mineral. In a deformational regime involving GBM accommodated dislocation creep, the recovery mechanism is GBM; dislocations are consumed as a grain boundary sweeps through a crystal (Poirier and Guillope 1979; Yund and Tullis 1991; Hirth and Tullis 1992; Stunitz 1998). Thus, r' may be expressed as a function of the velocity of GBM, v_{GB}, as follows:

$$r' = v_{GB} \cdot A_{GB} \cdot \left(d\sigma_i/d\rho_{dis}\right) \cdot \rho_{dis} \quad (16)$$

where A_{GB} is the grain boundary surface area expressed as area of grain boundary per volume of rock, σ_i is the internal stress, and ρ_{dis} is the dislocation density (units of total dislocation length/unit volume) of the material being consumed by the migrating grain boundary. Combining terms gives an expression for the GBMDC strain rate in terms of v_{GB}:

$$\dot{\varepsilon}_{GBMDC} = \frac{v_{GB} \cdot A_{GB} \cdot \left(d\sigma_i/d\rho_{dis}\right) \cdot \rho_{dis}}{h'} \quad (17)$$

Substituting for h' from the following expression—

$$h' = \frac{d\sigma_i}{d\varepsilon} = \frac{d\sigma_i}{d\rho_{dis}} \cdot \frac{d\rho_{dis}}{d\varepsilon} \quad (18)$$

[Eq. (4.18) in Poirier (1985)]—yields for the strain rate

$$\dot{\varepsilon}_{GBMDC} = v_{GB} \cdot A_{GB} \cdot \frac{d\varepsilon}{d\rho_{dis}} \cdot \rho_{dis} \qquad (19)$$

A similar expression may be written for the reaction in terms of the velocity of grain boundary migration. The rate of bulk reaction, or mineral "processing" through the intergranular medium, R (units of grams of solid reacted per gram of solid per time), will be equal to the velocity of grain boundaries sweeping through the solid, v_{GB}, scaled by A_{GB}:

$$R = v_{GB} \cdot A_{GB} \cdot \rho_{sr}/\rho_s \qquad (20)$$

where, here, ρ_{sr} is the density of the solid reactants and ρ_s is the average density of the bulk solid. Given the approximation that $\rho_{sr} = \rho_s$ and assuming that ρ_s does not change with time (i.e. $\Delta V_{rxn} = 0$), R and $\dot{\varepsilon}_{GBMDC}$ may be compared by means of these two equations:

$$R = \dot{\varepsilon}_{GBMDC} \Big/ \frac{d\varepsilon}{d\rho_{dis}}\rho_{dis} = \dot{\varepsilon}_{GBMDC}/K \qquad (21)$$

At steady state creep (for a given P,T), the dislocation density ρ_{dis} of mineral domains being consumed by migrating grain boundaries is a constant value. The constant of proportionality, K, between strain rate and reaction rate accounts for the efficiency by which strain may be accommodated internally by the production and motion of dislocations.

Based on this equation, if $K > 1$ (when the development of internal dislocations is not rate-limiting for GBMDC strain), the bulk strain rate will exceed the bulk reaction rate due to the contribution from internal dislocation development which has no bearing on the bulk reaction rate. This alone could account for the observation of Baxter and DePaolo (2002b) at Simplon Pass that the strain rate is faster than the reaction rate (Fig. 1), where GBM appears to have been important. However, given that there are likely to be additional contributions from group 2 strain mechanisms in the Simplon Pass rocks, it would be inappropriate to attribute the entire difference in reaction and strain rates to the constant K. If $K < 1$ (when the development of internal dislocations is rate limiting for GBMDC strain), then bulk reaction could proceed faster than GBMDC. Beyond this threshold, however, GBDC would be a more efficient strain mechanism than GBMDC. In this case, strain accommodation by GBDC would predominate and occur at a rate equal to or greater than the reaction rate (see Eq. 14).

The discussion above addresses the relative rates of reaction and GBMDC strain. The absolute rates of reaction and GBMDC strain are determined and controlled ultimately by v_{gb} (see Eqs. 19 and 20), which in turn depends on the available driving energy. Grain boundary migration may be driven by strain energies stored in dense dislocation tangles, by interfacial energies (typically a small contribution), and by any chemical potential energy promoting breakdown, intergranular transport, and reprecipitation of material. Regardless of the absolute contributions from these potential driving energies, the resulting grain boundary migration will accommodate both GBMDC and reaction. Stunitz (1998) shows that the contributions of chemical and strain energy to the total driving thermodynamic potential for grain boundary migration are additive. In general, the total driving energy, ΔG_{tot}, for the reaction and GBMDC strain rates will be the sum of the chemical energy, ΔG_{rxn}, and the strain energy, ΔG_{strain} (as well as interfacial and elastic energy which can usually be neglected). In the language of structural geology, v_{GB} may be expressed as a function both of the driving energy ΔG_{tot} (expressed as a driving force, F) and a "mobility" factor (Poirier 1985), which describes the inherent ease of, or resistance to, grain boundary motion. In the language of geochemistry, the "mobility" is broadly analogous to the "rate constant" k within a kinetic rate law (e.g. Wood and Walther 1983; Lasaga 1986; Baxter and DePaolo 2002b). The effective mobility (or rate constant) for grain boundary migration controlled strain *and* reaction may in turn be affected by the rate of grain boundary diffusion (i.e. reactant supply/transport rate), the temperature, the degree of boundary coincidence, or chemical characteristics such as pH, ionic species, or impurities. For the current purpose, because GBMDC strain and reaction are generally linked by the same grain boundaries (though, see next paragraph), the driving energy and mobility are the same for both processes and have no bearing on their *relative* rates, as indicated by their absence from Eq. (21).

A note on grain vs. phase boundaries

In the forgoing discussion, we have used the term "grain boundary" to include both boundaries between differently oriented grains of the same mineral and boundaries between different mineral phases A and B. The latter is often referred to as a phase boundary. It is surely the case that all of the individual grain (or phase) boundaries within the bulk rock may themselves be moving at different rates, depending on the absolute contributions from chemical, strain, and interfacial energies at each boundary. In general, grain boundaries between like minerals may be expected to migrate faster than phase boundaries as they do not have the potential limitation of long-scale intergranular diffusive transport of reactant or product species to or from the migrating phase boundary required to complete the net transfer reaction associated with converting phase A (and perhaps other reactants) to phase B (and perhaps other products). In such a case, that particular net transfer reaction (A + other = B + other) may be further limited and proceed *at an even slower rate* than GBMDC strain (which may be accommodated in the bulk rock mostly by grain boundary migration between like minerals) as compared to Eq. (21). Furthermore, while strain may be

accommodated by grain boundary movement between identical minerals where no meaningful reaction occurs, every grain (or phase) boundary whose bounding minerals participate in rock-wide chemical reactions will have an associated increment of strain accommodated as well. So, while strain and reaction may be decoupled at boundaries between identical minerals, such decoupling can only result in faster bulk strain than reaction, not the opposite.

A comment on possible heterogeneity of reaction within a rock

If a rock has a strongly heterogeneous mineralogy, it is conceivable that certain reactions may occur within discreet portions of the rock, while other portions of the rock react little or not at all. For example, consider the case of a pure quartzite with discreet nodules of carbonate. Reaction between quartz and carbonate to form wollastonite will occur only locally where the nodules exist. If only a small, inhomogeneously distributed portion of the rock is participating in reactions, then it is possible for the rate of those reactions to be decoupled from the rate of *bulk* strain. In our example, the local $quartz + calcite = wollastonite + CO_2$ reaction may occur rapidly, but deviatoric stresses could possibly be supported by minimal strain in rigid, non-reactive pure quartzite portions of the rock. This could allow rapid reaction to occur within pockets of a rock supported by a rigid scaffold of slowly deforming non-reactive rock. Thus in such cases, particularly regarding "corona" type reactions of the sort described in this paragraph and in the literature by Joesten (1983), Carlson and Johnson (1991), Milke and Heinrich (2002) and others, the relationships we have described between reaction and bulk strain may break down. This is part of the reason we have emphasized the idea of bulk reaction—when all (or most of) the rock is participating in reaction and/or the reacting phases are distributed homogeneously in the bulk rock at the grain scale.

Conclusion

Comparisons of naturally derived constraints on reaction rates and strain in dynamic regional metamorphic settings show that bulk reaction rates are similar to, and slightly slower than, bulk strain rates. Grain boundary migration accommodated dislocation creep (GBMDC) and grain boundary diffusion creep (GBDC) (i.e. pressure solution), two dominant plastic strain mechanisms in the crust and mantle, fundamentally involve dissolution and reprecipitation reaction of material after processing (and equilibrating) within the local ITM. When either process is active and controlling the rate of strain, reaction and strain rates are mechanistically linked. When GBDC is the more efficient strain controlling

mechanism then reaction and strain are related by Eq. (14). When GBMDC is the more efficient strain controlling mechanism, reaction and strain are related by Eq. (21). Furthermore, GBMDC and GBDC also involve other processes which may increase the total bulk strain rate (i.e. dislocation development and climb, and grain boundary sliding) without increasing the bulk reaction rate. Furthermore, when any other (i.e. group 2) strain mechanism is more efficient than either GBDC or GBMDC, strain and reaction rates are decoupled, and strain will be faster than reaction.

This relationship between reaction and strain rate applies so long as ΔG_{rxn} and ΔG_{strain} are both non-zero. For example, if $\Delta G_{rxn} = 0$, even if there is contributing energy from another source, i.e. deviatoric stress, there will be no net chemical consequences, though there may be isochemical processing of mineral components through the ITM. Or, in the absence of any deviatoric stress, even if significant chemical energy exists to drive reaction, there will be no observable bulk strain. Since there is virtually always a non-zero deviatoric stress in the dynamic Earth as plates move and orogenesis proceeds, dynamic metamorphic reaction rates in ductilely deforming rocks can in general never exceed strain rates (though consider the exceptions listed below).

There are a few potential exceptions to this general conclusion that we review below. Cases where reaction rate may be faster than bulk strain rate include:

1. In the brittle regime where strain may be accommodated entirely within brittle features, leaving effectively zero deviatoric stress within local portions of undeforming, yet reacting, rock.
2. Solid-state phase change reactions (i.e. kyanite-sillimanite-andalusite) where no introduction or transport of material in the ITM is necessarily required which could be decoupled from bulk strain (though strain related to ΔV_{rxn} would occur).
3. In general, if only a small inhomogeneously distributed portion of the rock is undergoing reaction, its rate would be decoupled from the bulk rock strain rate as deviatoric stress is supported by a rigid, non-reactive matrix.
4. In "corona" type reactions where reactants contact each other directly, the local reaction rate may initially exceed the rate of GBDC strain.
5. In any setting where deviatoric stress is zero, as may characterize portions of contact aureoles, particularly if brittle deformation occurs (see #1 above), but note that contact aureoles must themselves accommodate significant stresses induced by the emplacement, expansion, and contraction of the magma body.

It should not be surprising, therefore, that bulk reaction rates measured in nature are slightly slower than natural strain rates (Fig. 3). A general conclusion of this study is that measurements of natural strain rate will provide an upper bound on natural reaction rates in those same rocks. Based on the data presented in Fig. 3,

the current conclusion is that strain rates in dynamic metamorphic systems apparently exceed reaction rates within a factor of 10.

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