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Ethan F. Baxter

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Notes

Natural constraints on metamorphic reaction rates

ETHAN F. BAXTER

Boston University, Department of Earth Sciences, 685 Commonwealth Avenue, Boston, MA 02215, USA (e-mail: efb@bu.edu)

Abstract: Quantitative constraints on the rates at which metamorphic reactions proceed in nature are now available from several sources. Most common are predictions made on the basis of laboratory kinetic data. However, the applicability of such laboratory-based predictions has long been questioned and many observations in the field now suggest much slower rates. Here, published quantitative field-based constraints on high temperature (>400 °C) reaction rates are assembled from a variety of sources. Reaction rates attending regional metamorphism are four to seven orders of magnitude slower than most laboratory-based predictions. A general rate law for regional metamorphism has been derived which best describes these field-based data:

$$\log_{10}(R_{\text{net}}) \cong 0.0029T - 9.6 \pm 1$$

where R_{net} is the net reaction rate ($\text{g}/\text{cm}^2/\text{a}$) and T is temperature ($^{\circ}\text{C}$). At the same time, natural reaction rates attending contact metamorphism differ from laboratory-based predictions by less than two orders of magnitude, and are in close agreement at higher temperatures. Thus, while existing laboratory-based kinetic data may be judiciously applied to some contact metamorphic systems, laboratory-based kinetic predictions clearly misrepresent regional metamorphism. To explain this kinetic discrepancy, regional metamorphic reaction rates may be limited by slow intergranular transport due to comparatively limited (or transient) availability of aqueous fluid in the intergranular medium. The general field-based rate law may be applied to regional metamorphic, and other environments (i.e. ultrahigh pressure or ultrahigh temperature metamorphism), if similar system characteristics (mainly, low aqueous fluid content) can be inferred.

The concept of 'local equilibrium' in geological systems, formalized by J. B. Thompson (1959) and D. S. Korzhinskii (1959), has formed the basis for the interpretation of mineral assemblages in terms of the history of pressures, temperatures, fluid compositions, and ages which they record. Petrologists recognized early on (for example, see Turner & Verhoogen 1951) the importance of metamorphic reaction rates in influencing the mineralogical and chemical changes that occur during metamorphism, and in controlling whether or not the local equilibrium assumption would indeed be valid. In 1983, B. J. Wood and J. V. Walther presented a compilation of available laboratory-based kinetic data (Wood & Walther 1983) and derived a universal rate law for hydrothermal reactions which they applied to natural metamorphic conditions to predict rapid reaction timescales of hundreds to thousands of years in natural high temperature (400–700 °C) metamorphic systems. Since then, while much study has been devoted to lower temperature (25–300 °C)

kinetics, comparatively fewer additional laboratory-based kinetic studies have been published for high temperature metamorphic applications (these include Matthews 1985; Tanner *et al.* 1985; Schramke *et al.* 1987; Heinrich *et al.* 1989; Hacker *et al.* 1992; Dachs & Metz 1988; Lutge & Metz 1991, 1993; Jove & Hacker 1997; Winkler & Lutge 1999), and most of these studies generally indicate reaction rates similar to those predicted by Wood & Walther (1983). It has been largely on the basis of these relatively fast laboratory-derived reaction rates that local equilibrium among phases in metamorphic systems is often assumed (some recent examples include Bickle *et al.* 1997; Dipple 1998; Ferry & Gerdes 1998).

At the same time, a recognition has developed that not all laboratory-based experiments may be directly applied to natural systems (for example, see discussion in Rubie & Thompson 1985; Kerrick *et al.* 1991; Hacker *et al.* 1992; Jove & Hacker 1997; Baxter & DePaolo 2000, 2002*b*) because different rate-limiting mechanisms and

conditions apply, particularly for fluid-rich powder experiments which enhance transport of reactants to and from sites of reaction relative to coarser-grained fluid-poor systems such as may characterize much of the crust (the importance of fluids and grain size are discussed further below). Fluid-rich powder experiments constitute the bulk of the available published experimental data. Furthermore, natural effects that may be attributable to slower reaction rates and/or local disequilibrium have been identified (see below). Today, it is generally accepted that most laboratory-based kinetic predictions probably overestimate natural metamorphic processes because the rate-limiting mechanisms may vary. The outstanding question for which there is no generally accepted answer is: *by how much and in what circumstances* do laboratory-derived reaction rates overestimate natural reaction rates?

This question has increased in importance given the immense body of literature now available on the theory and application of integrated reactive transport modelling in geological systems – models within which some quantification of natural reaction kinetics is required. Modern studies of metamorphic or other high temperature processes requiring such quantification of reaction rates (some recent examples include Lasaga & Rye 1993; Barnett *et al.* 1996; Valley *et al.* 1997; Ague 1998; Ague & Rye 1999; Widmer & Thompson 2001; Balashov & Yardley 1998; Cui *et al.* 2002; Lasaga *et al.* 2000, 2001) refer to one of the aforementioned experimental studies, despite the possibility that these reaction rates may not accurately represent the natural systems which they model. This is certainly not done out of ignorance, but rather due to the lack of a comparable natural kinetic dataset with which the laboratory rates may be *quantitatively* compared, evaluated, and if necessary, replaced by a field-based value. Many modellers of high temperature systems (e.g. DePaolo & Getty 1996; Ague 1998; Lasaga *et al.* 2000, 2001) demonstrate the potential effects of varying reaction rates over several orders of magnitude: such effects are significant, but modellers have little basis by which to identify the most representative rate. In the field of low temperature geochemistry, in particular the study of the rates and processes of weathering, the discrepancy between laboratory-based and field-based kinetic predictions is very well known (e.g. White & Brantley 1995; Velbel 1993), and specific study in that field has been directed to reconcile and address this fundamental paradox. The same cannot be said of the field of metamorphic petrology, due in part to the

comparative difficulties in direct observations of nature and the problem of extrapolating observable processes to long timescales.

Today, the field of metamorphic petrology has evolved from analysis of static P–T conditions at given times in the history of the crust to an investigation of the rates, timescales and periodicities of the dynamic processes that shape it. Reaction and/or equilibration rates constitute an important and universal link between geochronological, thermodynamic, and petrographic interpretation of mineral assemblages. As such, given the key role of reaction kinetics in interpreting natural rocks, the importance of an improved understanding of field-based constraints on reaction rates is clear. Field-based quantifications of reaction rates are necessary in providing a ‘ground truth’ with which to evaluate the kinetic predictions of theory and laboratory-based data. Whereas several comprehensive reviews of laboratory-based kinetic data and the theory of extrapolating such data to natural systems have been published (e.g. Wood & Walther 1983; Rubie & Thompson 1985; Kerrick *et al.* 1991), no similar compilation of the field-based dataset on reaction rates is available. This paper assembles published *quantitative* field-based constraints on reaction rates attending high temperature metamorphism, extracted from a variety of sources, in order to illuminate the existence and consistencies (or lack thereof) of such field-based quantifications.

Reaction rate

When we speak of a reaction rate in a geological context, a variety of connotations may come to mind. We may be interested in the net reaction rate at which a particular chemical reaction proceeds towards equilibrium. Or, we may speak of the gross forward (and backward) reaction rates which compete and whose difference actually determines the rate of net reaction. For example, isotopic or cation/anion exchange responds to the gross reaction rates in a system, whereas the progress of a particular mineral-forming reaction depends on the net reaction rate. Mechanistically, there are a variety of processes that may influence or control reaction rates (e.g. nucleation, surface dissolution, intergranular transport, deformation) as discussed by many authors (e.g. Brodie & Rutter 1985; Rubie & Thompson 1985; Kerrick *et al.* 1991; Lasaga 1998). Despite these complexities, we can generalize the reaction process as one involving: (1) breakdown of mineral components; (2) the introduction of those components into the

intergranular medium which surrounds the minerals; (3) transport of some or all of those mineral components over some distance through the intergranular medium; and (4) reformation of minerals in a configuration and chemistry that, from a thermodynamic perspective, tends to minimize the total free energy of the system. In this paper, reaction rate will be expressed in terms of the amount of the bulk solid that has been reacted, per year, normalized by the surface area of the rate limiting mineral (see Lasaga 1998) in the particular reaction process (units of $\text{g}/\text{cm}^2/\text{a}$). For sake of simplicity, use of these units implies that the reaction rate and rate-limiting surface area are both constant in time, neither of which is likely to be the case. Milke & Metz (2002), for example, argue against normalization to reactant surface area due to such complexities. Therefore, reaction rates expressed this way represent time-averaged reaction rates. Generalized this way, the process of 'bulk reaction' allows us to compare a range of mechanisms that, while they may vary in their rate-limiting properties or driving forces, share the basic description outlined above.

Laboratory-based predictions

It is not the endeavor of this paper to provide a detailed critique of all available laboratory-based kinetic data. For that, the reader is referred to the individual studies cited below, or to literature reviews of experimental data (e.g. Rubie & Thompson 1985; Kerrick *et al.* 1991). However, to provide a basis of comparison for the natural reaction rates that will be discussed, let us quickly review the laboratory-based kinetic data appropriate for high temperature (>400 °C) metamorphic systems. Fig. 1 and Table 1 show a summary of such data published since, and including, the study of Wood & Walther (1983). Because the various studies express results for different reactions, perhaps for different mechanisms, and in various forms, including a variety of rate laws, direct comparison of these data is not straightforward. It is assumed that all rate laws, while defined for a particular reaction, may be compared by using them as a general expression for any metamorphic reaction. In Fig. 1, the various laboratory-based data are compared by expressing each in terms of the net reaction rate, R_{net} (in units of $\text{g}/\text{cm}^2/\text{a}$), as determined from each rate law. To maintain consistency and generality, net rates of reaction for all rate laws including a dependence on ΔG_{rxn} , were calculated (and plotted in Fig. 1) for the same range of $|\Delta G_{\text{rxn}}|$ from 80 J (representative of a 1 °C overstep of a metamorphic dehydration

reaction ($\Delta S_{\text{rxn}} = 80 \text{ J/K}$; $-\Delta G_{\text{rxn}} = \Delta S_{\text{rxn}}(T - T_{\text{eq}})$), after Wood & Walther 1983) to 5600 J (representative of a 70 °C overstep (also assuming $\Delta S_{\text{rxn}} = 80 \text{ J/K}$), as suggested by Baxter & DePaolo 2002b). This range in ΔG_{rxn} is arbitrary, and is not intended to correspond to the actual ΔG_{rxn} realized in the laboratory experiments for each individual reaction. Rather, this range is shown to include ΔG_{rxn} that may characterize a wide range of metamorphic reactions, and a wide range of equilibrium oversteps as we are not focusing here on any particular reaction. For the Winkler & Lutge (1999) data, the four net reaction rate data they present in their Table 3 are shown. The study of Tanner *et al.* (1985) differs from the others in that they determined a diffusion-controlled rate law, independent of ΔG_{rxn} , but dependent on time, and hence on the amount of reaction progress α . Using their diffusion-controlled rate law, a representative range of net reaction rates was calculated by monitoring $d\alpha/dt$ from $\alpha = 0.1$ to $\alpha = 0.9$. Finally, data from Cole (1992) and Cole & Chakraborty (2001) on the rate of chemical reaction-controlled, (i.e. dissolution-precipitation) oxygen isotope exchange are included in Table 1 and Fig. 1. These data are not expressed as a function of ΔG_{rxn} , and thus the range of experimentally derived values was plotted directly. Because isotopic exchange rates depend on the gross reaction rates, these may generally be faster than the net reaction rates shown for metamorphic reactions, but, for $\Delta G/RT > 0.1$ (see Baxter & DePaolo 2002a) this difference is less than a factor of 10. Listed in Table 1 but not pictured in Fig. 1 is the non-linear rate law of Lasaga (1986) fitted to the data of Schramke *et al.* (1987). As discussed in Baxter & DePaolo (2002a), this non-linear fit is not a good representation of the Schramke *et al.* (1987) data for small values of ΔG , and therefore is misleading for the current purpose. At higher values of ΔG (800–4000 J), the non-linear fit to the Schramke *et al.* (1987) data does yield net rates plotting within the 'S-L' box as shown in Fig. 1.

While all of these rate laws were derived from a wide range of reactions and processes, with the exception of the lower temperature Tanner *et al.* (1985) data, they all predict a fairly consistent range of reaction rates, spanning no more than three orders of magnitude for a given temperature (and ΔG_{rxn}) and increasing slightly with temperature. For a natural reactive surface area of $20 \text{ cm}^2/\text{g}$, representative of 100 μm radius spheres with 20% by volume of the rate-limiting mineral, this corresponds to natural net reaction rates of $c. 10^0\text{--}10^{-3} \text{ a}^{-1}$ (for $T = 600$ °C)

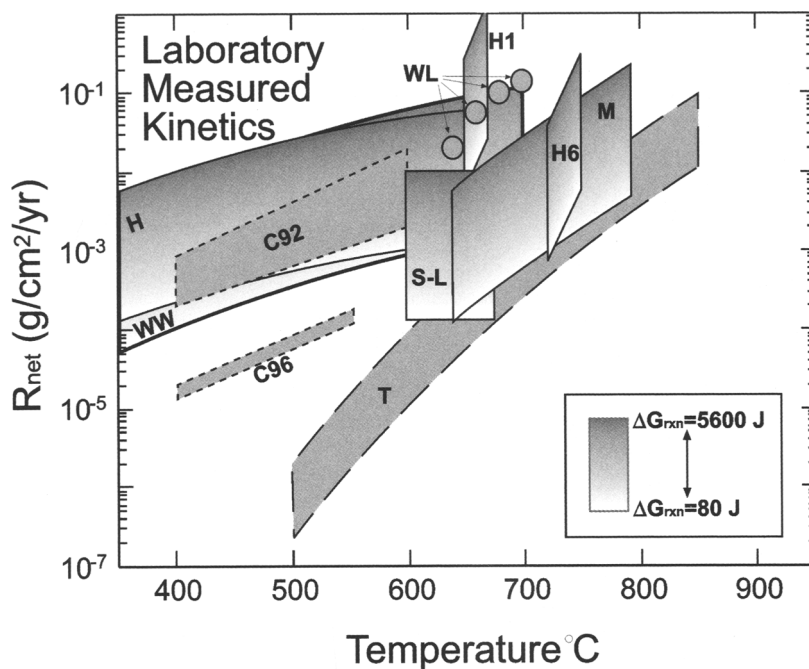


Fig. 1. Reaction rates predicted by laboratory experiments summarized in Table 1. Shown are relevant kinetic data for high temperature ($>400\text{ }^{\circ}\text{C}$) metamorphic systems published since (and including) the 1983 Wood & Walther compilation. Data are plotted only for the range of temperatures over which experiments were actually conducted. Gradationally shaded solid-lined regions represent net reaction rate predictions for ΔG_{rxn} ranging from 80 J to 5600 J as discussed in the text following the respective rate laws in Table 1. Circles (WL) represent individual data points from Winkler & Luttge (1999). Coarse dashed box (T) represents rates of Tanner *et al.* (1985) after reaction progress, α , of 0.1 (top line of box) to 0.9 (bottom line of box). Fine dashed box (C92) represents the oxygen isotope exchange data for NaCl molality ranging from 4 M (top line of box) to 0 M (bottom line of box). Note that the vertical range of each data box does not indicate experimental error, but rather the range in net rate predicted for different values of ΔG , α , and molality, respectively. Fine dashed box (C96) represents single data points for the temperature range: height of this box is arbitrary. See text for details. Abbreviations refer to the data in Table 1: C92, Cole (1992); C96, D. R. Cole (1996, unpublished); H, Helgeson *et al.* (1984); H1, Heinrich *et al.* (1989: $\text{XCO}_2 = 0.1$); H6, Heinrich *et al.* (1989: $\text{XCO}_2 = 0.6$); M, Matthews (1985); S-L, Schramke *et al.* (1987: linear rate law); T, Tanner *et al.* (1985); WL, Winkler & Luttge (1999); WW, Wood & Walther (1983).

which in turn suggests reaction timescales ($1/R$) of $c. 1\text{--}1000$ years. If such rates in fact represent natural systems, equilibrium (or at least a steady state; Lasaga & Rye 1993; Lasaga *et al.* 2001) would be reached on those timescales.

Other experimental studies have demonstrated that rates and mechanisms achieved in the laboratory setting may not necessarily be applicable in natural settings and geological timescales. A major issue is the difference in fluid content between the relatively fluid-rich powder experiments and the comparatively fluid-poor conditions which may characterize a significant proportion of the crust undergoing metamorphism (e.g. Thompson 1983; Rubie & Thompson 1985; Rubie 1986). Hacker *et al.* (1992) performed experiments on solid polycrystalline marble (no fluid added) to study

the calcite to aragonite transformation rate. They concluded that the rate, and mechanism, for this reaction is much slower than, and different from, analogous experiments employing powders or single crystals. They further speculate that kinetic hindrance of metamorphic reaction progress in natural systems in general may extend to high temperatures ($>200\text{ }^{\circ}\text{C}$) if net reaction is limited by intergranular transport and/or fluid content. Jove & Hacker (1997) determined that the experimental rate of the breakdown of laumontite (in fluid-rich powder experiments) was far too fast to be consistent with observation of natural rocks where laumontite is preserved. Again, possible reasons suggested for this difference include slow nucleation rate, slow intergranular transport due to lower fluid content, and slower heating/cooling rate in natural cases. Experiments

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Table 1. Recent laboratory-based kinetic data for metamorphic reaction/exchange

| Reference | Abbrev. | Reaction* | Experimental temperatures (°C) | Rate law† | k in rate law | k units |
|--|---------|---|--------------------------------|---|---|---|
| Wood & Walther (1983) | WW | Metamorphic reactions | 25–700 | $R_{\text{net}} = k \cdot (-\Delta G/RT)$ | $\log(k) = \frac{-2900}{T} - 6.85$ | gram-atoms O/cm ² /s |
| Helgeson <i>et al.</i> (1984) | H | K-feldspar dissolution | 25–650 | $R_{\text{net}} = k \cdot$ $[1 - \exp(-\Delta G/RT)]$ | $k = 10^{-11.8} \cdot T \cdot$ $\exp(-4250/T)$ | mol/cm ² /s |
| Matthews (1985) | M | Zoisite breakdown | 635–792 | $R_{\text{net}} = k \cdot$ $[1 - \exp(-\Delta G/RT)]$ | $k = 32.2 \cdot$ $\exp(-22900/T)$ | g/cm ² /s |
| Tanner <i>et al.</i> (1985) | T | Calcite + quartz = wollastonite + CO ₂ | 500–850 | $R_{\text{net}} = \frac{1}{2} + \frac{k^{1/2}}{t}$ | $k = 7.7 \times 10^{-2} \cdot$ $\exp(-27100/T)$ | (g/cm ²) ² s ⁻¹ |
| Schramke <i>et al.</i> (1987) (linear: Lasaga & Rye 1993, eqn. 48) | S-L | Muscovite + quartz = andalusite + sanidine + H ₂ O | 600–675 | $R_{\text{net}} = k \cdot \Delta G$ | $k = 3.3 \times 10^{-16}$ | mol/cm ² /s J/mol |
| Schramke <i>et al.</i> (1987) (non-linear: Lasaga 1986, eqn. 28) | S-N | Muscovite + quartz = andalusite + sanidine + H ₂ O | 600–675 | $R_{\text{net}} = k \cdot \Delta G^{2.68}$ | $k = 4.38 \times 10^{-22}$ | mol/cm ² /s (J/mol) ^{2.68} |
| †Heinrich <i>et al.</i> (1989) | H1 | Tremolite + dolomite = forsterite + calcite + CO ₂ + H ₂ O | 650–670 | $R_{\text{net}} = k \cdot$ $[1 - \exp(-\Delta G/RT)]$ | $k = 9.37 \times 10^{24} \cdot$ $\exp(-69600/T)$ | g/cm ² /s |
| †Heinrich <i>et al.</i> (XCO ₂ = 0.1) | H6 | Tremolite + dolomite = forsterite + calcite + CO ₂ + H ₂ O | 720–750 | $R_{\text{net}} = k \cdot$ $[1 - \exp(-\Delta G/RT)]$ | $k = 1.25 \times 10^{23} \cdot$ $\exp(-72500/T)$ | g/cm ² /s |
| Winkler & Lutge (1999) | WL | Tremolite + calcite + quartz = diopside + CO ₂ + H ₂ O | 640–700 | $R_{\text{net}} = k$ | 0.20 – 1.4 × 10 ⁻¹ | g/cm ² /a |
| Cole (1992) | C92 | Calcite –H ₂ O oxygen isotope exchange via reaction | 400–600 | $\log R = -4.19 - \frac{655.78}{T} - \frac{0.201}{m} - \frac{814.25(\log p_{\text{H}_2\text{O}})}{T}$ | na | R units: moles O/m ² /s |
| §Cole (1996, unpublished) | C96 | Muscovite –H ₂ O oxygen isotope exchange via reaction | 400–550 | $R_{\text{net}} = 1.5 \times 10^{-5} \cdot (-63800/RT)$ | na | R units: moles O/m ² /s |

*Rate-limiting mineral in bold, where applicable.

†Units of R_{net} are quantity (in moles, grams, or gram-atoms oxygen) reacted per square centimetre of the rate-limiting mineral per time.‡ k of Heinrich *et al.* (1989) corrected by factor of 100 to account for their use of percentage reaction rather than fractional reaction.

§See Cole & Chakraborty (2001, Table 2, entry #112).

by Lutge & Metz (1991, 1993) on both powders and natural rock cylinders (mixed CO₂-H₂O fluid added to both) showed that the reaction dolomite + quartz = diopside + CO₂ proceeds at a similar rate and mechanism in powder experiments and within discreet 'microsystems' of the natural rock cylinders. However, in *bulk*, the rock cylinder experimental kinetics were slower, and limited by transport of Si-species in the water-poor portions of the intergranular medium, in contrast to the more evenly distributed water in the powder experiments.

Field-based observations

In the last decade, many field-based studies have presented observations which could be due to much slower reaction rates than laboratory-based predictions discussed above would suggest. Here, we review this evidence and, where possible, describe the quantitative constraints that may be extracted about the absolute rates of reaction attending natural metamorphism. These are summarized below and in Table 2 in chronological order of publication, divided into constraints from regional and contact metamorphic systems. As necessary, total reaction rates in units of a⁻¹ were normalized to the surface area of the rate-limiting mineral using the average surface area of the matrix minerals, assuming an average rock density of 3 g/cm³, and assuming (arbitrarily) that 20% of the matrix constituted the rate-limiting reactant. The reactive surface area probably changes during metamorphism, but the assignment of a constant reactive surface area is a necessary simplification for the current purpose of comparison. Grain size information for each of the field studies is given in the Appendix.

Every effort was made to include the full range of available quantitative constraints existing in the published literature. However, as this compilation reflects the background and interests of the author, it is acknowledged that some work from which a quantitative constraint on reaction rates might be extracted may not have been included. Nevertheless, it is the author's hope and intent that the range of natural data presented here is representative of what has been extracted from natural observations up to the present time.

Constraints on reaction rate from regional metamorphic systems

Quantitative textural analysis of garnet porphyroblast distributions. Carlson *et al.* (1995)

present the results of garnet porphyroblast growth modelling from three different regional metamorphic systems (MD, Mica Dam; PM, Picuris Mountains; WR, Whitt Ranch). The modelling follows from quantitative textural analysis of garnet-rich metamorphic rocks, in particular exploiting the spatial distribution and crystal size distribution of garnets to extract quantitative information on garnet nucleation rate and diffusion-controlled growth rate. Carlson (2002), Lasaga (1998), Joesten (1991) and references therein describe the evidence and theory for diffusion-controlled reaction processes. The largest uncertainty in the analysis of Carlson *et al.* (1995) is the estimate for prograde heating rate, which they set at 10 °C/Ma, a reasonable value for prograde regional metamorphism within the predictions of thermal-tectonic models (e.g. 5–20 °C/Ma; England & Thompson 1984). The uncertainty associated with the possible deviation from this heating rate is less than an order of magnitude.

The progress of the diffusion-controlled garnet-forming reaction is strongly time-dependent as increasing temperature, increasing crystal radii, and increasing number of nuclei all change and affect the bulk reaction rate. To extract a representative range of reaction rates (in units of g/cm²/a) from the Carlson *et al.* (1995) data for the current purpose, equation 2a of Carlson *et al.* (1995) was used:

$$R_{\text{dpl}}(t) = \left(\int_{t_i}^t D_{T(t)} dt \right)^{1/2} \quad (1)$$

where R_{dpl} is the radius about each growing crystal centre that has been 'depleted' of garnet-forming nutrients: that is, reacted.

Using crystal densities in crystals per cubic centimetre ranging from 10% to 100% of the reported final values to account somewhat for progressive nucleation (MD, 7.2 crystals/cm³; PM, 231.4 crystals/cm³; WR1, 83.5 crystals/cm³; Carlson *et al.* 1995) and constant temperatures (Table 2) ranging from the reported onset of garnet growth to the metamorphic peak, the total fractional volume reacted, $(\frac{4}{3}\pi R_{\text{dpl}}^3)/\text{cm}^3$, was monitored in time, and the resulting range in instantaneous reaction rate (in a⁻¹) was extracted after 10% and 90% reaction progress had occurred. This approach does not include the rigorous treatment of progressive nucleation (included in the complete numerical scheme of Carlson *et al.* 1995), but it serves as a good representation of the range of possible rates. The ranges shown in Table 2 represent the maximum

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Table 2. Natural constraints on metamorphic reaction rates

| Reference | Abbrev. | Temperature (°C) | Metamorphic context | Reaction | Reaction rate (a ⁻¹) | Reaction rate* (g/cm ² /a) |
|-------------------------------------|---------|------------------|--------------------------------|--|--|--|
| †Carlson <i>et al.</i> (1995) – MD | CMD | 550–655 | Regional | Diffusion-controlled garnet growth | 0.52–20 × 10 ⁻⁷ | 1.0 × 10 ⁻⁸ –4.0 × 10 ⁻⁷ § |
| †Carlson <i>et al.</i> (1995) – PM | CPM | 435–525 | Regional | Diffusion-controlled garnet growth | 0.20–10 × 10 ⁻⁷ | 5.0 × 10 ⁻¹⁰ –2.5 × 10 ⁻⁸ §§ |
| †Carlson <i>et al.</i> (1995) – WR1 | CWR | 500–600 | Regional | Diffusion-controlled garnet growth | 0.44–19 × 10 ⁻⁷ | 1.7 × 10 ⁻⁹ –7.1 × 10 ⁻⁸ §§ |
| ‡Christensen <i>et al.</i> (1989) | C89 | 550–600 | Regional | Garnet-forming | 0.5–3.7 × 10 ⁻⁷ | 0.25–1.9 × 10 ⁻⁸ §§ |
| ‡Vance & O’Nions (1992) | VO | 480–530 | Regional | Garnet-forming | 1.6–16 × 10 ⁻⁷ | 0.16–1.6 × 10 ⁻⁸ §§ |
| ‡Christensen <i>et al.</i> (1994) | C94 | 455–475 | Regional | Garnet-forming | 1.0–6.2 × 10 ⁻⁷ | 0.33–2.1 × 10 ⁻⁸ §§ |
| Eppel & Abart (1997) | na | 250–300 | Regional | Quartz–fluid oxygen isotope exchange | ≥ 3 × 10 ⁻⁸ | ≥ 6 × 10 ⁻¹¹ ¶ |
| Skelton <i>et al.</i> (1997) | na | 400–530 | Regional – infiltration driven | amphibole + epidote + H ₂ O + CO ₂ = chlorite + calcite + quartz | na | 10 ⁻⁸ –10 ⁻³ |
| ‡Vance & Harris (1999) | VH | 570–700 | Regional | Garnet-forming | 2.2–7.2 × 10 ⁻⁷ | 1.5–4.8 × 10 ⁻⁸ §§ |
| Baxter & DePaolo (2002, 2002b) | BD | 630–480 | Regional | Bulk solid–fluid Sr isotope exchange plagioclase is rate-limiting | 1.4 ^{+1.1} _{-0.4} × 10 ⁻⁷ | 7.0 ^{+5.5} _{-2.0} × 10 ⁻⁹ |
| Joesten & Fisher (1988) (25 m) | JF | 840–940 | Contact | Diffusion-controlled quartz + calcite = wollastonite + CO ₂ | na | c. 3 × 10 ⁻² |
| Joesten & Fisher (1988) (49 m) | JF | 720–820 | Contact | Diffusion-controlled quartz + calcite = wollastonite + CO ₂ | na | c. 2 × 10 ⁻² |
| Joesten & Fisher (1988) (74 m) | JF | 630–730 | Contact | Diffusion-controlled quartz + calcite = wollastonite + CO ₂ | na | c. 5 × 10 ⁻³ |
| Joesten & Fisher (1988) (99 m) | JF | 600–650 | Contact | Diffusion-controlled quartz + calcite = wollastonite + CO ₂ | na | c. 2 × 10 ⁻³ |
| ‡Stowell <i>et al.</i> (2001) | na | 590–735 | Contact | Garnet-forming | ≥ 1.3–4.2 × 10 ⁻⁷ | ≥ 0.33–1.1 × 10 ⁻⁸ §§ |
| Waters & Lovegrove (2002) | WL | 540–560 | Contact | Andalusite growth | na | 7 × 10 ⁻⁵ –3 × 10 ⁻⁴ |

*Normalized to the geometric surface area of the rate limiting mineral, if applicable.

†Letters stand for the specific field site described; see Carlson *et al.* (1995).

‡Calculated from published garnet growth durations following Baxter & DePaolo (in press).

§Assumed 20% of total matrix surface area given in Appendix was of rate-limiting mineral reactant.

¶Rate is for quartz–fluid exchange only, so mode of quartz is not a factor.

(from T_{\max} , 90% reaction progress, 100% final crystal density) and minimum (from T_{\min} , 10% reaction progress, 10% final crystal density) of these extracted rates. The actual grain size attending garnet growth in the WR1 sample is obscured by post-garnet growth formation of a fine grained symplectite in the matrix; however, outlines of original grains can be discerned and do permit a rough estimate of the matrix grain size used in surface area normalization of the reaction rate (W.D. Carlson, pers. comm.; see Appendix).

Oxygen isotope disequilibrium. Eppel & Abart (1997) documented grain scale disequilibrium between minerals and fluids on the basis of systematic carbon and oxygen isotopic fronts across a tectonic contact in eastern Switzerland. They note an apparent systematic shift in quartz–calcite oxygen isotope fractionations across the isotopic front which they explain as the result of slow quartz–fluid oxygen isotope exchange. Abart & Sperb (1997) developed reactive transport models which were used to extract quantitative information on relative rates of quartz–fluid exchange kinetics, transport velocities, and duration of the fluid–rock interaction. However, they are unable to provide a firm constraint on the absolute quartz–fluid exchange rate because it is difficult to estimate absolute transport velocities or durations. They do note that, for a *maximum* possible duration of fluid–rock interaction (20 Ma) the rate of quartz–fluid exchange would be $3 \times 10^{-8} \text{ a}^{-1}$ (or $6 \times 10^{-11} \text{ g quartz/cm}^2 \text{ quartz/a}$ for 40 μm diameter grains), orders of magnitude slower than the laboratory-based predictions for oxygen isotope exchange in fluid-rich systems of Cole & Ohmoto (1986). This value is only a minimum constraint on reaction rates: if durations were shorter, the reaction rate would increase proportionally. It is also worth noting that, while quartz–fluid exchange appeared to be slow, calcite–fluid exchange was comparatively rapid. Abart & Pozzorini (2000) and Barnett & Bowman (1995) describe other field settings where similar effects attributable to kinetically limited isotope exchange are observed.

Modelling reaction progress within a metamorphosed sill. Skelton *et al.* (1997) measured patterns of reaction progress patterns across a metamorphosed sill in the Dalradian of Scotland which had been infiltrated by carbonate fluids from the surrounding country rock. Reactive transport modelling was used to extract non-dimensional parameters (i.e. Damkohler number) relating transport and reaction rates.

Analysis of these results suggested that the apparent reaction rates were at least one order of magnitude slower than that predicted by the laboratory-based data of Wood & Walther (1983). Considering a wide range of possible porosities and wetted surface areas, the authors determine a range of possible net reaction rates that is one to six orders of magnitude slower than the rate predicted by Wood & Walther for equivalent conditions. Skelton *et al.* (1997) suggest that this apparent difference may result from slow diffusional transport from fluid channels where bulk transport was most efficient.

Bulk solid–fluid Sr isotope exchange. Baxter & DePaolo (2000, 2002b) documented patterns of Sr isotopic diffusional transport about a lithologic contact near Simplon Pass, Switzerland, that also suggest local fluid–rock disequilibrium due to slow reaction. Measurement of whole rock and garnet Sr isotope ratios along a sample traverse provide information on a synmetamorphic initial condition (from garnet) and final condition (from whole rocks) after metamorphic exchange ceases. Independent garnet and plagioclase geochronology constrains the timescale over which the observed Sr isotopic exchange occurred (13.2 Ma) – information which is crucial in obtaining an accurate measure of the absolute reaction rate. Reactive-transport modelling allows determination of the absolute local bulk solid–fluid reaction rate within the system. Ultimately, the magnitude of the isotopic step preserved in the whole rocks at the lithologic contact determines the reaction rate (see Baxter & DePaolo (2002a) for full discussion). The bulk Sr exchange rate ($1.4_{-0.4}^{+1.1} \times 10^{-7} \text{ a}^{-1}$) reflects the sum of all reaction processes among the system phases, driven not by the Sr isotope variations, but by the total affinity for reaction. In these rocks, metapelites and meta-amphibolites, plagioclase is the dominant Sr-bearing phase, and thus serves as the rate-limiting mineral for Sr exchange between the bulk solid and the intergranular transporting medium. Thus normalizing by the plagioclase surface area, the deduced rate is $7.0_{-2.0}^{+5.5} \times 10^{-9} \text{ g/cm}^2/\text{a}$.

Constraints from published garnet growth durations. 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) from several locales including Townshend Dam, Vermont (Christensen *et al.* 1989), the Steinental area, Switzerland (Vance & O’Nions 1992),

Tauern Window, Austria (Christensen *et al.* 1994), Zanskar, Himalaya (Vance & Harris 1999) and Wrangell, Alaska (Stowell *et al.* 2001), the latter being a contact metamorphic occurrence. Baxter & DePaolo (in press) describe a method by which crude, yet representative, reaction rates may be extracted from these growth durations. To do this, Baxter & DePaolo (in press) assume that the garnet-forming reaction has gone to between 50% and 90% completion, probably a reasonable range for most situations. That garnet growth has not gone to 100% is supported by the lack of observed slowing in progressive garnet growth rates within single porphyroblasts, and the observation that garnets forming in different bulk compositions from the same locality cease to grow at the same time (Christensen *et al.* 1989, 1994; Baxter & DePaolo in press). Using the following equation

$$\frac{\% \text{ completion}}{100} = 1 - e^{-R\Delta t} \quad (2)$$

where Δt is the duration of garnet growth, Baxter & DePaolo (in press) obtain a net reaction rate for garnet formation (in a^{-1}). Results of these calculations for the five published garnet durations referenced above are shown in Table 2.

Net reaction rates derived from garnet growth durations are crude estimates, not only because they require an arbitrary estimate of reaction progress, but also because these reactions occur over a wide range of changing conditions. Just as the analysis of Carlson *et al.* (1995) showed that the rate of garnet-forming reaction may vary by as much as two orders of magnitude over the history of their growth, the same is probably true of these garnets. Furthermore, the possibility that garnet growth was not continuous over the entire interval encompassing garnet formation cannot be ruled out, though available age profiles in large garnet porphyroblasts (Christensen *et al.* 1989, 1994; Vance & O'Nions 1992; Vance & Harris 1999) are more indicative of continuous growth. Thus, while the deduced ranges for these garnet studies may not represent all of the uncertainty, the rates nonetheless are representative of the time-averaged reaction rates for the various locales. The fact the garnet reaction rates from regional metamorphic systems (abbreviated C89, VO, C94, VH in Fig. 2) appear to be in close agreement with the other reaction rate constraints from regional metamorphic systems is encouraging.

Strain rate data. Many studies have investigated the possible links between strain and

reaction, including instances where strain enhances reaction and vice versa (e.g. Brodie & Rutter 1985; Rubie & Thompson 1985; Yund & Tullis 1991; Stunitz 1998; Steffen *et al.* 2001). Baxter & DePaolo (in press) have presented arguments that, for rocks undergoing plastic strain during metamorphism, the bulk strain rate represents an upper limit for the bulk reaction rate of mineral phases in the same rock. The argument stems from the fact that reaction – involving the breakdown, transport, and reformation of mineral components – will occur concomitantly with bulk strain, by either pressure-solution (i.e. diffusion creep) or by grain-boundary-migration accommodated dislocation creep strain. The rates of bulk reaction and strain may be linked by these common processes or, because strain may additionally be accommodated by other means (such as grain-boundary sliding), the rate of reaction typically will not exceed the rate of strain in systems experiencing plastic strain. Exceptions to this rule would include phase transformations where no extragranular transport necessarily occurs, though some volume change and associated strain will inevitably accompany a phase change. The other exception is any system which is not undergoing any plastic strain; that is, a system for which there is zero local deviatoric stress, perhaps due to strain accommodation only in discrete fractures or shear zones. This situation may describe some contact metamorphic environments, though there must be some significant strain associated with emplacement of the magma body and its thermal relaxation. Commonly observed reaction coronas in apparently strain-free deep crustal rocks (e.g. Johnson & Carlson 1990; Carlson & Johnson 1991 and references therein) may also present a case of zero local deviatoric stress (and hence, zero strain) during the corona-forming reaction.

Table 3 shows strain rate estimates from a variety of studies, discussed in more detail in Baxter & DePaolo (in press) and the associated references. These limits are not shown in Fig. 2 for clarity (they would plot at rates no more than an order-of-magnitude faster than the associated garnet reaction rates), and because most are accompanied by garnet growth duration data as described above which provides a more direct constraint.

Constraints on reaction rate from contact metamorphic systems

Contact metamorphism occurs over much shorter timescales than typical regional metamor-

phism and as such must exhibit generally faster rates. The relatively faster rates attained in contact systems may be due to increased fluid content generated by the rapid reactions and from the intruding magma itself, higher temperatures, and large ΔG_{rxn} resulting from rapid heating rates.

Diffusion-controlled growth of reaction rims. Joesten & Fisher (1988) present an analysis of diffusion-controlled growth of wollastonite rims on chert nodules within the Christmas Mountains contact aureole. They review thermal modelling of the evolution of the aureole by Joesten (1983) and use the thickness of reaction rims as a function of distance from the intrusion to extract information about the diffusion-controlled growth history. Using the reaction-rim thickness history for four different samples shown in figure 17 of Joesten & Fisher (1988) and the thermal history shown in figure 3 of Joesten (1983), average reaction rates have been extracted here in terms of grams of wollastonite produced per surface area of chert nodule per year. For this calculation, a 50 mm diameter spherical chert nodule was used, representative of those in figure 8 of Joesten & Fisher (1988). As with any diffusion-controlled process, the rate varies strongly with time, and in this case is very rapid in the earliest stages where enormous driving energies exist due to the rapid spike in temperature imposed on the system. Here, the rate from each sample was determined by considering the temperature–time interval starting with $T_{\text{peak}} - 100^\circ\text{C}$ until T_{peak} for each sample, with the exception of the sample at $x = 99$ m because growth does not begin until 600°C . Rates thus derived represent time-averaged reaction rates after the incipient stages of contact metamorphism. Other studies of broadly similar rim or coronal growth exist from which some constraint on reaction rates could possibly be derived (e.g. Carlson & Johnson 1991; Ashworth *et al.* 1998 and references therein), but the thermal history presented by Joesten (1983) provides an opportunity to extract

quantitative constraints without assumptions of reaction duration, and thus is presented here as the representative of rim-growth studies in general.

Textural analysis and grain size distributions. Waters & Lovegrove (2002) showed evidence for disequilibrium and significant reaction overstepping from textural analysis of metapelites from the Bushveld contact aureole in South Africa. Analysis of nucleation history and crystal size distribution suggests that the net reaction rate characterizing the system was at least one order of magnitude slower than comparable laboratory-based predictions (Schramke *et al.* 1987). Waters & Lovegrove (2002) determined reaction overstepping on the order of 40°C , resulting in the importance of metastable reactions in the sequence of mineral growth. From figure 10 of Waters & Lovegrove (2002), a range of 1×10^{-6} to 4×10^{-6} is extracted for the pre-exponential constant, k^+ . This value may be used in a rate law of the general form:

$$R_{\text{net}} = k^+ \cdot \exp(-Ea/RT) \cdot [1 - \exp(-\Delta G/RT)] \quad (3)$$

where $Ea = 56\,000\text{ J}$ and $\Delta G = 5000\text{ J}$, also from figure 10 of Waters & Lovegrove (2002). The resulting range in net reaction rate is 7×10^{-5} to 3×10^{-4} in g andalusite/cm²/a.

Summary of natural constraints on reaction rate

Figure 2 shows the field-based reaction rate data plotted together with the laboratory-based reaction rates shown for comparison. Several observations are worthy of mention. First, the contact and regional metamorphic datasets, respectively, define distinct ranges of reaction rate as a function of temperature, but differ from each other significantly. The contact metamorphic dataset, albeit based on only two field

Table 3. Strain rates from rotated garnet porphyroblasts

| Reference | Locale | Growth duration (Ma) | Strain rate (a^{-1}) |
|----------------------------------|---------------------------|----------------------|---|
| Christensen <i>et al.</i> (1989) | Vermont, USA | 10.5 ± 4.2 | $7.6^{+5.0}_{-2.2} \times 10^{-7}$ |
| Vance & O'Nions (1992) | Swiss Alps | 2.9 ± 1.5 | $6.0 \pm 2.8 \times 10^{-7}$ |
| Christensen <i>et al.</i> (1994) | Tauern Window, Austria | 5.4 ± 1.7 | $8.5^{+3.8}_{-2.2} \times 10^{-7}$ |
| Baxter & DePaolo (in press) | Simplon Pass, Switzerland | $1.4\text{--}3.4^*$ | $0.3 \times 10^{-6} - 1.0 \times 10^{-6}$ |

*Growth duration estimated from range of published radial growth rates.

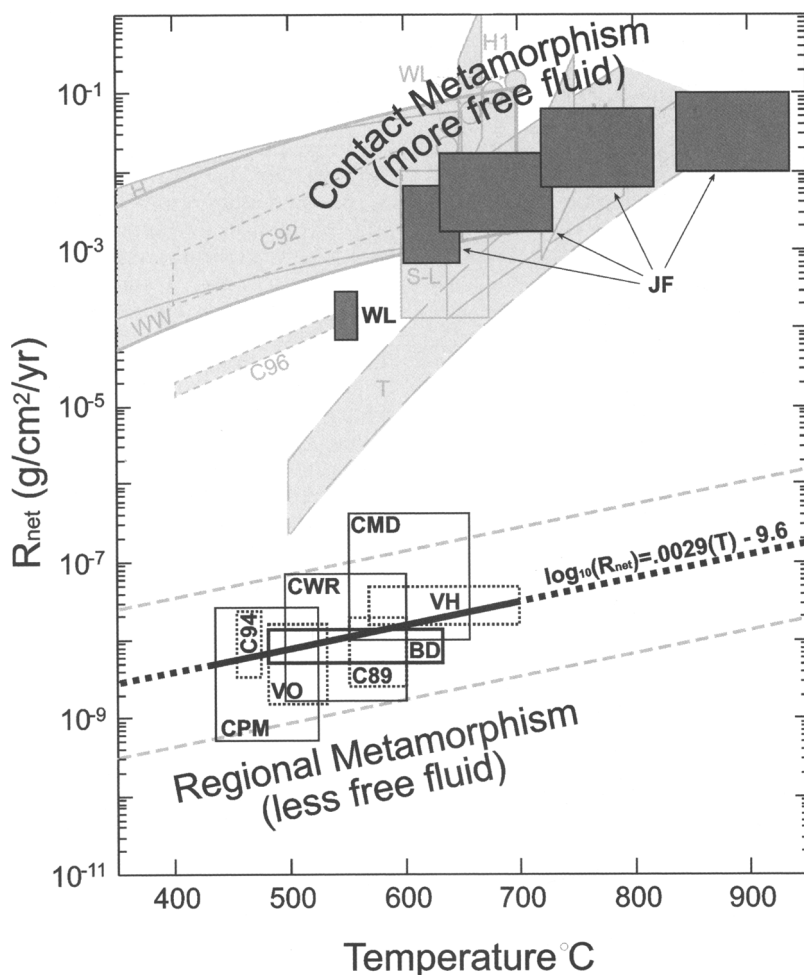


Fig. 2. Natural constraints on high temperature ($>400\text{ }^{\circ}\text{C}$) metamorphic reaction rates. Abbreviations refer to the data in Table 2. Contact metamorphic constraints are shown as dark shaded boxes: JL, Joesten & Fisher (1988); WL, Waters & Lovegrove (2002). Unshaded boxes represent constraints from regional metamorphic systems. Dashed boxes represent reaction rates derived from direct garnet growth rate measurements: C89, Christensen *et al.* (1989); C94, Christensen *et al.* (1994); VH, Vance & Harris (1999); VO, Vance & O’Nions (1992). Thick-lined open box represents bulk solid–fluid Sr isotope exchange rate: BD, Baxter & DePaolo (2000, 2002*b*). Thin-lined boxes represent constraints from modelling of crystal size and spatial distributions for diffusion-controlled growth of garnets (CMD, CPM, CWR; Carlson *et al.* 1995). Each of the Joesten & Fisher (1988) data points from Table 2 are given an arbitrary one-order-of-magnitude error envelope. Ranges for the other data are described in the text. The best-fit line describing all of the regional metamorphic data is shown in bold, with \pm one order-of-magnitude uncertainty depicted in grey dashed lines. The discrepancy between regional and contact metamorphic reaction rates probably relates to differences in fluid content. Laboratory-based data from Figure 1 are shown in light grey.

studies, demonstrates a trend of increasing rates with increasing temperature from *c.* $10^{-4}\text{ g/cm}^2/\text{a}$ at $550\text{ }^{\circ}\text{C}$ to *c.* $10^{-1}\text{ g/cm}^2/\text{a}$ at $940\text{ }^{\circ}\text{C}$. These rates coincide fairly well with much of the experimental data, particularly for the higher temperature data from the Joesten & Fisher (1988) study. Given the rapid heating rates, and consequent large temperature oversteps creating

large ΔG_{rxn} , characterizing contact systems (i.e. 5000 J estimated by Waters & Lovegrove 2002) the appropriate comparison is to the upper portion of each laboratory-based box (in Fig. 2) reflecting such large ΔG_{rxn} . Thus, the high temperature data of Joesten & Fisher (1988) appears to be within about one order of magnitude of analogous laboratory-based pre-

dictions, whereas the Waters & Lovegrove (2002) 550 °C constraint is about two orders of magnitude slower than the predictions of Wood & Walther (1983) or Helgeson *et al.* (1984), but within the full range of experimental data including the muscovite–fluid oxygen isotope exchange data of D. R. Cole (1996, unpublished) and the diffusion-controlled kinetic data of Tanner *et al.* (1985). Based on these results, it appears that much of the existing laboratory-based kinetic data predict the actual reaction rates in contact metamorphic systems reasonably well, and may therefore be judiciously employed in the modelling and interpretation of contact metamorphic systems, though the effects of reaction rates up to two orders of magnitude slower should be considered.

The picture is very different for regional metamorphic reaction rates. Here, the data define a trend of increasing R_{net} from *c.* 10^{-9} to *c.* 10^{-7} g/cm²/a for temperatures increasing from 450 to 700 °C. The fact that all of the natural data agree so closely suggests that the three methods of extracting natural reaction rates presented are probably reasonably correct, and furthermore, that the range of natural regional metamorphic reaction rates probably lies within this narrow range. This well-constrained range of values from natural systems is many orders of magnitude slower than most of the experimental data. Only the Tanner *et al.* (1985) data (for a diffusion-controlled reaction mechanism) for lower temperatures comes within two orders of magnitude of the actual natural reaction rates; all other laboratory-based kinetic data overestimate natural reaction rates by four to seven orders of magnitude.

A simple linear relation between R_{net} and temperature (similar in concept to the relation proposed by Wood & Walther (1983) based in their case on laboratory data) may be fitted to the data, giving equal weight to the extremes of all data ranges. This general expression for regional metamorphic reaction kinetics has the form:

$$\log_{10}(R_{\text{net}}) = 0.0029T - 9.6 \quad (4)$$

This relation carries with it an uncertainty of at least an order of magnitude (Fig. 2), particularly if extrapolating beyond the temperature range of the data presented. However, when modelling a regional metamorphic reaction, this equation provides a far better estimate of the actual natural reaction rate than any of the laboratory-based rate laws. This rate law (equation 4) may be employed to estimate natural reaction rates attending any system with fundamental characteristics (perhaps

most notably fluid content, see below) similar to the regional metamorphic systems plotted in Figure 2.

Clearly, existing laboratory-based reaction rates grossly misrepresent natural regional metamorphic systems, as many have suspected. Slow reaction kinetics will result in *higher* ΔG_{rxn} as disequilibrium grows. Baxter & DePaolo (2002*b*) estimate temperature overstepping of up to 70 °C (and on the order of 5600 J ΔG_{rxn} , depending on $\Delta S_{\text{rxn(P,T)}}$ for the specific reaction) due to slow reaction rates during regional metamorphic heating of 10 °C/Ma. Most importantly, these slow natural reaction rates confirm that equilibrium may not necessarily be achieved in regional metamorphic systems. Failure to reach equilibrium will adversely affect any of the range of interpretive geochemical tools (e.g. geothermobarometry, fluid or chemical flux calculations based on reaction progress, isochron geochronology, stable isotope thermometry) based on the local equilibrium assumption.

At the same time, it cannot be overlooked that there are many other examples of natural studies where the condition of local equilibrium does appear to have been reached (for example, any case where reasonable and/or corroborated interpretations of P–T–time based on the local equilibrium assumption is achieved). Recall that the requirement for local equilibrium (Korzhinskii 1959; Thompson 1959) is simply that the rate at which the local phases of interest, or at least certain separable portions of those phases, were able to react and exchange with their surroundings at a rate *exceeding the local rates of change* of the intensive system parameters: P–T–X, including isotopic compositions. Interpretations of such assemblages in terms of P–T of equilibrium, isotopic ages, fluid chemistry etc. should be accurate. Attainment of local equilibrium need not depend on the absolute reaction rate – only on the rate sufficiently exceeding that of local P–T–X change. Indeed, Lasaga & Rye (1993) showed that even with relatively ‘fast’ laboratory-based reaction kinetics, a disequilibrium ‘steady state’ may characterize certain dynamic systems. Conversely, even with relatively slow reaction kinetics, if P–T–X also changes slowly, local equilibrium may still be attained. The important point is that, even given that absolute bulk reaction rates are very slow, if reasonable care is taken in sample collection and petrographic analysis, useful data may still be derived, often by the use of microanalysis of rims of mineral phases (presumed to represent equilibrium compositions) as is so commonly done. In order to recognize where or when we might

encounter problems applying the local equilibrium assumption, we must know the local bulk reaction rate in order to compare it to the rates of P–T–X change we might expect to characterize a particular environment. This should include open system mass transport considerations on the hand-sample to outcrop scale during sampling.

Possible causes for the discrepancy between contact metamorphic and regional metamorphic kinetics

The large discrepancy between reaction rates in regional metamorphic systems v. those in contact metamorphic systems (and all the laboratory-based data) merits further discussion. Many studies (e.g. Thompson 1983; Rubie & Thompson 1985; Ridley & Thompson 1986; Kerrick *et al.* 1991; Jove & Hacker 1997; Baxter & DePaolo 2002*b*; Carlson 2002) have discussed a range of possibilities why reactions in nature might proceed at different rates (or mechanisms) than in the laboratory, and the reader is referred to such works for complete discussion. A major difference between laboratory powder experiments and nature, is the grain size of reactants. But this factor has been normalized out in the presentation of data in this paper (except for the potential effects of surface roughness; Helgeson *et al.* 1984). The importance of the magnitude of the driving energy for reaction ΔG_{rxn} has also been discussed, and accounted for within the various laboratory-based rate laws used in Figs 1 and 2. Differences in ΔG_{rxn} of about a factor of 1000 could potentially exist in nature – in large part due to variable heating rates and temperature overstepping (Ridley & Thompson 1986) – but, unless different functional forms (e.g. linear v. non-linear) of the dependence on ΔG_{rxn} apply in the laboratory (and contact metamorphism) as opposed to in regional metamorphism, this cannot account for the four to seven order of magnitude discrepancy depicted in Fig. 2. The remainder of the discussion will focus on two key, ultimately related, system properties which typically differ between contact and regional systems: intergranular transport rate and fluid content.

Intergranular transport

Many studies (e.g. Carmichael 1969; Fisher 1978; Ridley & Thompson 1986; Kerrick *et al.* 1991; Bickle 1992; Lasaga 1998; Carlson 2002, and references therein) have discussed the

importance of the transport of reactant and product species in limiting the overall bulk reaction rate (i.e. transport- or diffusion-limited reaction). Such transport is accommodated typically by diffusion within the intergranular transporting medium (i.e. the IGR of Brady 1983; or the ITM of Baxter & DePaolo 2002*a*) which is the fluid, melt or ‘dry’ grain boundary between the minerals of a rock. On small scales, the ITM may be quite heterogeneous, but it may often be reasonable to assume that, over some sufficiently large averaging volume, the transporting properties of the ITM may be assigned as a single bulk property of a rock or system (Brady 1983). For example, Skelton *et al.* (1997) suggest that bulk reaction may be limited by slow transport of reactants away from fluid channels with characteristic spacing on the order of centimetres, meaning an averaging volume of less than 1 cm would result in spatially variable and fundamentally different bulk reaction properties than an averaging volume of much greater than 1 cm. Reactions rate-limited by a grain boundary migration mechanism (e.g. Baxter & DePaolo 2002*b*) may in turn be limited by the rate of reactant transport to and from the bounding surfaces of the migrating grain boundary. Ultimately, a reaction rate may be limited by the slowest moving (usually via diffusion) of its reactant species, which may be Si or Al in many systems (e.g. Carmichael 1969; Spear & Daniel 2001; Carlson 2002; Milke & Heinrich 2002, and others). The most important property of the ITM in determining intergranular transport rate is the fluid, or more specifically, water content.

Fluid content

It is well known that the abundance of fluids in a given system can greatly affect the rates at which intergranular transport and reaction occur. An ITM that is entirely wetted by a free fluid (as opposed to structurally bound water in minerals or tight grain boundaries; Rubie 1986) will permit much faster diffusion than an ITM that is devoid of free fluid. As discussed by many authors (e.g. Rubie & Thompson 1985; Ridley & Thompson 1986; Kerrick *et al.* 1991 and others), the fluid-rich environments created in the laboratory are different from nature, and hence could contribute to the apparent difference in rates. Fluid content appears also to affect volume diffusivities measured in the laboratory which can contrast markedly with apparent effective volume diffusivities actually attending comparatively dry metamorphic environments (e.g. Villa & Puxeddu 1994; O’Brien 1999; Cooke *et al.*

2000). Recent study has focused on the wetting behaviour of fluids (e.g. Watson & Brenan 1987; Holness 1995; Skelton *et al.* 1997; Hiraga *et al.* 2001). Watson & Brenan (1987) showed that carbonate-rich fluids tend to wet mineral surfaces much less than water-rich fluids. Indeed, Heinrich *et al.* (1989) showed that laboratory reaction kinetics were significantly slowed in the presence of a more CO₂-rich fluid. Such observations suggest that not just amount of fluid, but also fluid content (i.e. water content) is important in reaction kinetics. The possibility that fluids may be present within rocks only over transient periods of time – much shorter than the duration of the entire metamorphic event – has also received considerable attention (e.g. Thompson 1983; Young & Rumble 1993; van Haren *et al.* 1996; Connolly 1997; Graham *et al.* 1998). If fluid availability in the ITM is limited to only a small fraction of the total metamorphic duration, then the apparent reaction rates on metamorphic timescales would be proportionally slower. Reaction and equilibrium in such a case would proceed in short spurts, interspersed with long periods of little or no reaction, and consequent disequilibrium. It continues to be the case that quantification of the periodicity of fluid availability in geological systems is a frontier worth pursuing in crustal geochemistry and petrology.

Contact metamorphic environments typically are regarded as being more consistently fluid rich in comparison to regional, or deeper crustal ultrahigh temperature (UHT) or ultrahigh pressure (UHP) metamorphism. For example, consider the fact that *time-integrated* fluid fluxes in contact metamorphic systems are equal to (or greater than) those in most regional metamorphic systems (e.g. Ferry & Gerdes 1998), despite the fact that the integration times (i.e. duration of metamorphism) differ by several orders of magnitude. There are at least two reasons for this. First, contact metamorphic environments, by definition, are related to a local hot igneous body, which itself provides a significant flux of volatiles as it is replenished, degasses and cools. Second, the duration of the entire metamorphic heating event is shorter. It is more likely that fluids generated by dehydration reactions *and* from the degassing magma will remain at higher levels in the ITM during the short-lived contact event characterized by rapid temperature increase than over the longer-lived gradually evolving regional event (Thompson 1983). Of course, local variations in fluid content due to fluid focusing along cracks or shear zones (e.g. Thompson 1983, 1987; Brenan 1991; Selverstone *et al.* 1991; Dipple & Ferry 1992; Ague

1994) are quite likely in both contact and regional systems. However, the conclusion may reasonably be stated that contact metamorphism generally involves a 'wetter' ITM than regional metamorphism, more like the fluid-rich laboratory-based experiments with which contact metamorphic kinetics appear to more closely agree.

Implications for UHP/UHT systems

The preservation of relict UHP and UHT minerals and textures as well as various isotopic studies have been used to argue for slow reaction rates due to 'dry' conditions in these settings (e.g. Hacker & Peacock 1995; Scaillet 1996; Liou *et al.* 1997; Zhang & Liou 1997; O'Brien 1999; Zheng *et al.* 2002) though actual quantifications of absolute reaction rates have thus far been difficult to obtain. If the lack (and/or distribution) of fluid characterizing UHP/UHT systems is similar to (or even more extreme) than the regional metamorphic systems shown in Figure 2, and rate-limiting mechanisms are also similar (which has not been demonstrated), then equation 4 would provide a good description, or at least an upper limit, for bulk reaction rates in UHP/UHT environments. This constraint may prove particularly useful for studies regarding the effects of progressive metamorphism of subducting slabs where debate has focused particularly on the extent to which the slab has converted to eclogite (e.g. Ahrens & Schubert 1975; Hacker 1996; Abers 2000; Connolly & Kerrick 2002). For example, using equation 4, a gabbro with 50% by volume, 1 mm radius plagioclase grains (5 cm²/g) at 700 °C would have a reaction rate of *c.* 1.3 × 10⁻⁷ a⁻¹. Employing equation 2 to describe the progress of reaction, this means that more than *c.* 15% of the original gabbro would persist at those conditions for at least 15 Ma (i.e. 2/R_{net}). Even as fluids are created during slab dehydration, unless fluid contents exceed those in the typical regional metamorphic environments depicted in Figure 2, reaction rates in subducting slabs probably do not exceed this limit. As such, even this crude kinetic constraint should be useful. The confidence with which equation 4 may be applied to such varied metamorphic systems (i.e. UHP/UHT) will be illuminated only by studies confirming or refuting mechanistic similarities between these environments, improved quantification of free fluid contents and its effects, and additional field-based reaction rate data derived from a wider range of conditions than presently available.

Summary

The field-based constraints on metamorphic reaction rates assembled here allow *quantification* of the magnitude of the often-predicted discrepancy with laboratory-based reaction rates. The discrepancy is less than two orders of magnitude for contact metamorphic systems, but as much as seven orders of magnitude in regional metamorphic systems – a profound difference. At the same time, the limited amount of well-constrained field-based kinetic data from a range of conditions, prevents us at this time from establishing truly universal kinetic laws, and/or rate parameters, that may be directly applied to any natural system. To accommodate the need for a realistic and accurate kinetic treatment of natural systems in our models and interpretations, it is clear that we must move beyond the use of laboratory-based data alone, and beyond the simple acknowledgement that reaction rates in nature are ‘probably much different’ than in the laboratory. To do this, an effort needs to be made to fill out the *quantitative* natural kinetic dataset, using new methods or techniques following on from those reviewed here. Kinetic data must be sought from a variety of environments including varying lithology, temperature, strain history, fluid content, or inferred reaction mechanisms in order to define and quantify the controlling factors in nature. In light of the importance of water content in this regard, a quantitative parameterization of the effects of P(H₂O) (i.e. the amount of free H₂O in the ITM; Rubie 1986) should continue to be an important part of future research endeavors. As such new field-based data are accumulated, it will also be helpful to express reaction rates with units easily extrapolated, or compared, to other data or other mechanisms. As discussed above and shown in Figures 1 and 2, the author favours the expression of bulk reaction rates in terms of grams reacted per square centimetre of the rate-limiting mineral per year (g/cm²/a). These units effectively normalize out the different molecular weights of reactants (similar to the gram-atom-oxygen normalization used by Wood & Walther 1983) and the use of ‘grams’ provides an easily applicable physical quantity in modelling. The noted variability in reactive surface area with time as well as the possibility of transient reaction processes means that this reaction rate expression is a time-integrated average. When analysing rocks which themselves reflect the total time-integrated metamorphic history, for many applications, such a time-integrated reaction rate will be of greatest utility.

While this paper has focused on the natural dataset, the full understanding of natural reaction

kinetics will come only with carefully integrated field and laboratory-based study, cemented by theory. With additional guidance and ‘ground-truthing’ provided by field-based kinetic data, we may then return to the laboratory to design experiments appropriate for examining the factors and mechanisms that matter most in nature. To overcome some of the limitations of past powder experiments in particular, further exploration of laboratory studies employing natural rocks as starting materials (e.g. Hacker *et al.* 1992; Lutge & Metz 1993) may be particularly useful. In fact, a significant amount of experimental work on natural and/or coarse-grained material has already been conducted, but most remains unpublished given the lack of systematic results and the difficulties with scaling issues inherent in such work (A. B. Thompson, pers. comm.). Overcoming the challenges of these time-scaling issues when designing innovative experiments to emulate nature will continue to be a major obstacle.

In the meantime, this paper has illuminated a more accurate range of reaction rates that should be used in the modelling and interpretation of natural metamorphic systems. For contact metamorphic systems, particularly for higher temperatures, the laboratory-based data should suffice as a reasonable value, overestimating the actual rate by less than two orders of magnitude. For regional metamorphic systems, the simple rate law:

$$\log_{10}(R_{\text{net}}) \cong 0.0029T - 9.6 \pm 1$$

fitted here to the range of natural kinetic data, should be used. Note that this rate law does not assume any knowledge of the ΔG_{rxn} attending the system, only that the ΔG_{rxn} (including how it may vary during the reaction history), and other characteristics, of the field-based systems plotted in Figure 2 represent good averages for regional metamorphism in general. At the very least, it behoves the geochemist to consider the effects of the documented range of field-based reaction kinetics in models and interpretations as quantitative data now exist.

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Appendix*Matrix grain size and surface area information used in reaction rate normalization*

| Reference | Matrix grain size and material | Reference | Calculated average total matrix surface area (cm ² /g)* |
|------------------------------------|--|---------------------------------------|--|
| Baxter & DePaolo (2000, 2002b) | c. 200 µm diameter plagioclase | Baxter & DePaolo (2002b) | 100 |
| Christensen <i>et al.</i> (1989) | 400 × 200 µm strained quartz grains 600 × 80 µm mica discs | E. F. Baxter (personal samples) | 100 |
| Vance & O'Nions (1992) | 200 × 30 µm strained quartz grains | D. Vance (pers. comm.) | 500 |
| Christensen <i>et al.</i> (1994) | 200 × 40 µm strained quartz grains 400 × 50 µm biotite discs | J. Selverstone (pers. comm.) | 150 |
| Vance & Harris (1999) | 1250 × 200 µm strained quartz grains | D. Vance (pers. comm.) | 75 |
| Stowell <i>et al.</i> (2001) | c. 100 µm diameter grains | Stowell <i>et al.</i> (2001, Fig. 3a) | 200 |
| Eppel & Abart (1997) | 40 µm diameter quartz | Eppel & Abart (1997) | 500 |
| Carlson <i>et al.</i> (1995) – MD | 2800 × 1200 µm strained quartz grains 1600 × 400 µm biotite discs | W. D. Carlson (pers. comm.) | 25 |
| Carlson <i>et al.</i> (1995) – PM | 10–200 µm diameter grains | Chernoff & Carlson (1997) | 200 |
| Carlson <i>et al.</i> (1995) – WR1 | c. 150 µm diameter original grains | W. D. Carlson (pers. comm.) | 133 |

*An average mineral density of 3.0 g/cm³ was used in all surface area calculations.

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