ESTIMATES OF DIFFERENTIAL STRESS LEVELS IN THE EARTH

It should be borne in mind that all these estimates are snapshots of differential stresses varying in time and space. All indirect methods are based on assumptions which must be assessed carefully, and even in a single study different stress estimates may not agree. For example Masuda et al. (2011) found stress levels differing by a factor of 10 using two different techniques; they attribute this to the diagnostic microstructures being formed at different times.

Table DR1. Some estimates of differential stress in the Earth, and the methods used.

Δσ (MPa)	**Where**	**Method**	**Reference**
<10	Oman, upper crust	Halite subgrain size	(Schoenherr et al., 2010),
9-15	Blueschist facies, Syros	Microboudinage of glaucophane	(Masuda et al., 2011)
~12	Tonale line, 560 °C	Quartz recrystallized grain size (Twiss calibration)	(Stipp et al., 2002)
30	Mid crust, Papua New Guinea	Quartz recrystallized grain size	(Little et al., 2007)
~40	Tonale line, 440 °C	Quartz recrystallized grain size (Twiss calibration)	(Stipp et al., 2002)
20-70	Mid crust, Bohemia	Quartz recrystallized grain size	(Zulauf, 2001)
129-141	Blueschist facies, Syros	Calcite twinning	(Masuda et al., 2011)
135±70	Ivrea zone	Dislocation density in mylonitic minerals	(Kenkmann and Dresen, 2002)
170	Deepest boreholes	Direct measurement	(Zoback and Townend, 2001)
~200	Tonale line, 300 °C	Quartz recrystallized grain size (Twiss calibration)	(Stipp et al., 2002)
200-400	Sesia zone (eclogite facies continental crust)	Jadeite twins etc.	(Kuster and Stockhert, 1999)
220-580	Corsica	Calculated from volume of pseudotachylytes	(Andersen et al., 2008).

GENERAL THEORY OF HOW STRESS AFFECTS REACTION AFFINITY

Here I show how in general, though depending on reaction pathway, the effect of varying differential stress will be greater than the effect of varying a single uniform pressure by the same amount. Consider a general balanced reaction, possibly involving fluids, written as

$$\sum_{m=1}^{N} c_m X_m + c_f X_f = 0$$

where X_i is the chemical formula of mineral i, or fluid, and c_i indicates the number of moles of i, or fluid. The sign of c_i for solids indicates whether that solid is dissolving (> 0, a reactant) or precipitating (< 0, a product). Let μ_i be the chemical potential of phase i (strictly the chemical potential of a chemical component equivalent to the composition of i). Let mineral i dissolve or precipitate at an interface across which the normal stress is σ_i: this depends on the reaction pathway. The affinity for that pathway is then

$$A_{path} = \sum_{m=1}^{N} c_m \mu_m(\sigma_m) + c_f \mu_f(P_f) \qquad \text{(S1)}$$

If A > 0, the products are favoured. In other words if the reactant phases are present in a rock then there is a driving force for reaction along that pathway. We consider situations in which there are just three normal stresses involved: σ_1, σ_3 and P_f the pore fluid pressure. Specifying a functional dependence of σ_3 and P_f on σ_1 then allows us to calculate A as a function of T and σ_1 and find the A = 0 contour. Whether the pathway is actually effective depends on the kinetics of diffusion and attachment and detachment of atoms from lattices at interfaces.

Such calculations are sufficient to plot "threshold" affinities for reactions along various pathways such as on Figs. 2 and 3. However useful insight is gained by considering why the effects of differential stress are so large, as follows

If stress is isotropic and equal to pressure P on all phases, then all normal stresses are equal to P and

$$A = \sum_{m=1}^{N} c_m \mu_m(P) + c_f \mu_f(P)$$

The sensitivity of A to P is quantified via

$$\partial A / \partial P = \sum_{m=1}^{N} c_m V_m + c_f V_f(P) \equiv \Delta V \qquad \text{(S2)}$$

which is the net volume change in the reaction. Now consider a rock under differential stress and define a pathway where minerals 1..L dissolve or precipitate at interfaces under normal stress σ_1 whilst L+1..N dissolve or precipitate at interfaces under normal stress σ_3. Then

$$A_{path} = \sum_{m=1}^{L} c_m \mu_m(\sigma_1) + \sum_{m=L+1}^{N} c_m \mu_m(\sigma_3) + c_f \mu_f(P_f)$$

For a reaction not involving water (or keeping P_f fixed)

$$\partial A_{path} / \partial \sigma_3)_{\sigma_1} = \sum_{m=L+1}^{N} c_m V_m \qquad \text{(S3)}$$

There is a range of values possible here, depending on pathway: the extreme values are equal to the total volume of reactant solids (when all $c_m > 0$), and the total volume of product solids (when all $c_m < 0$). Thus in the new theory the affinity depends on differential stress via a quantity of the order of molar volume V (eqn. S3) whilst in conventional thermodynamics the

affinity depends on pressure via the volume *change* ΔV (eqn. S2). Since ΔV is generally much smaller than V, differential stress generally has a much greater effect than changing pressure. Table DR1 indicates volume changes for some reactions not involving fluid, expressed as percentages relative to the smaller molar volume side of the reaction, calculated using the Thermocalc database of (Powell and Holland, 1988) for illustrative conditions of 600 °C and 500 MPa. For reactions involving fluid, suppose we have a single confining pressure, and $\sigma_3 = P_f$, so

$$\partial A_{path} / \partial P_f)_{\sigma_1} = \sum_{m=L+1}^{N} c_m V_m + c_f V_f \qquad \text{(S4)}$$

Again we can compare this value with ΔV (Table DR2). The ratio V/ ΔV serves to epitomise the importance of differential stress in metamorphism according to these new calculations.

Table DR2. Assemblage volume and volume change for a selection of metamorphic reactions

Reaction	(volume change)/ (volume of denser assemblage) %	(volume of denser assemblage)/(volume change) = Stress sensitivity
Solid-solid reactions		
1 py + 1 di + 1 q = 2 en + 1 an	11.5	8.7
1 ky = 1 sill	12.2	8.19
1 ab = 1 jd + 1 q	20.4	4.9
1 alm + 3 ru = 1 ky + 3 ilm + 2 q	7.3	13.7
1 gr + 2 ky + 1 q = 3 an	27.1	3.68
Dehydration reactions		
1 atg = 4 ta + 18 fo + 27 H2O	9.9	10.1
1 atg = 14 fo + 10 en + 31 H2O	9.9	10.1
1 mu + 1 q = 1 san + 1 sill + 1 H2O	10.1	9.9
6 mu + 2 phl + 15 q = 3 crd + 8 san + 8 H2O	17.0	5.88
1 mu + 3 clin + 3 q = 1 phl + 4 py + 12 H2O	3.1	32.26
6 fst + 25 q = 8 alm + 46 ky + 12 H2O	0.32	308.8

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