ENHANCED DISSOLUTION OF MINERALS:
STORED ENERGY, AMORPHISM AND MECHANICAL ACTIVATION

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ABSTRACT

A theoretical evaluation of the origin and role of stored energy in the phenomenon of mechanically-activated dissolution of finely milled minerals has been undertaken. The changing mechanical behaviour of minerals with decreasing particle size is examined, leading to the treatment of stored energy in terms of the generation and retention of crystalline imperfections (dislocations) during extended milling. Development of amorphism, and polymorphism, is treated as a direct consequence of decreased periodicity in the crystal lattice that is associated with an increased accumulation of dislocations. Quantitative estimates of stored energy are presented and used to quantify changes in dissolution kinetics in terms of a decreased activation energy of dissolution and hence, an increase in the relative rate of dissolution.

Keywords
Communion; grinding; particle size; leaching; reaction kinetics

INTRODUCTION

Mechanical activation is generating interest as a pre-treatment process prior to the leaching of minerals (Baláž, 2000). The process involves prolonged milling to produce finely-ground particles that exhibit enhanced dissolution rates additional to the effects of increased specific surface area on dissolution. A previous theoretical study by the authors (Tromans and Meech, 1999) showed that surface microtopography plays an important role in mechanically-activated dissolution of particles in the micron to sub-micron range, due to the higher rate of reaction at step edges relative to planar surfaces (terraces). The present work is a continuation of our fundamental analysis of mechanical activation effects. In this paper, we are primarily concerned with the influence of stored energy and the development of amorphism (non-periodic regions) in the mineral lattice, both of which have been linked in a general, non-formalised manner to mechanically-activated dissolution (Tkáčová et al., 1993; Baláž et al., 1996, 2000; Welham, and Llewellyn, 1998; Maurice and Hawk, 1999; Baláž, 2000). For completeness, the influence of stored energy on polymorphic transitions is also included in the analysis.

Initially, we characterise the fundamental mechanical behaviour of minerals as particle size decreases and then assess the resulting effects on the generation of imperfections that control stored energy and transitions to amorphous or polymorphous phases. Subsequently, we estimate the increased chemical free energy per mol due to these imperfections and transitions, and apply these results to an analysis of changes in the activation energy and kinetics of dissolution.
PARTICLE SIZE AND MECHANICAL BEHAVIOUR

The classical energy balance studies of Griffith (1920) on the propagation of a small crack (flaw) in an elastically isotropic solid established a functional relationship between the critical tensile stress \( \sigma_c \) for crack propagation and flaw size, \( a \), having the general form:

\[
\sigma_c \propto \sqrt{\frac{E \gamma}{a}}
\]

(1)

where \( E \) is the tensile elastic modulus and \( \gamma \) is the surface free energy.

Equation (1) was derived on the basis that the rate of elastic strain energy released during crack propagation was equal to the work required to generate new surface area accompanying crack extension. The analysis was conducted for an ideal brittle solid where inelastic atom displacements (plasticity) in the crack tip region were absent. Other workers recognised that such ideal behaviour does not apply to the majority of crack-sensitive materials and the surface energy term in Equation (1) should be replaced by an energy function that accounts for crack-tip plasticity effects (Irwin 1948, Orowan 1955). Such modifications, applicable where crack tip plasticity is confined to a small plastic enclave in an elastic matrix, have led to the recasting of Griffith’s ideas in terms of fracture mechanics concepts:

\[
K_{IC} (1 - v^2) = (E \gamma / (2a))^{1/2}
\]

(2)

where \( K_{IC} \) is the critical stress intensity for crack propagation under Type I conditions (opening mode), \( \gamma \) is the corresponding critical energy release rate per unit area of crack plane (equivalent to \( 2\gamma \) for ideal brittle fracture and >\( 2\gamma \) for real materials), and \( v \) is Poisson’s ratio. [N.B. Inclusion of the \( (1 - v^2) \) term implies plane strain conditions, which is replaced by unity for plane stress conditions.]

The value of \( K_{IC} \) has the general form:

\[
K_{IC} = Y \sqrt{(a)}^{1/2}
\]

(3)

where \( Y \) is a geometrical factor related to the shape of the crack, e.g. \( Y \) has the value \((\pi a)^{1/2}\) for a straight through internal crack of length \( 2a \) and the value \( 2(\pi a) \) for an internal penny-shaped (disc-shaped) crack of radius \( a \) (Broek, 1982).

A general feature of crack-sensitive crystalline materials, including minerals, is that they exhibit small amounts of plasticity via dislocation generation and movement during mechanical testing. For example, Gilman (1958) has listed sixteen non-metallic crystals that exhibit dislocation generation (plasticity) during cleavage crack propagation, including minerals such as galena, calcite, gypsum, dolomite and orthoclase. Also, dislocation generation has been detected around hardness test indentations on ceramic single crystals, such as perovskite (\( \text{Na}_{0.75} \text{WO}_3 \)) and \( \text{MgO} \) (McCohn, 1990).

Application of Equations (2) and (3) to minerals containing a size distribution of flaws (cracks) allows changes in mechanical behaviour to be assessed as particle size decreases during comminution. In particular, these equations show that a decreasing flaw size \( a \) requires higher tensile stresses for a crack to propagate, \( \sigma_c \propto (a)^{-1/2} \). Hence, initial fracture and size reduction of minerals occurs via propagation of the largest flaws at relatively low \( \sigma_c \). As milled particle size decreases, only small flaws remain and these must be less than the particle diameter. Consequently, increased loading stresses must be imposed to generate further particle fracture via propagation of the remaining flaws. At this point, it is recognised that impact between colliding surfaces during milling produces compressive loads on particles. However, the irregular shape of milled particles ensures that each impact is confined to a local surface area so that a localised elastic strain field is produced that is within a relatively unstrained matrix. The high local compressive stress \( (\sigma_p) \) produced by impact causes an elastic contraction (compression) in the particle parallel to \( \sigma_p \) and a lateral elastic extension normal to \( \sigma_p \) via Poisson’s ratio \( (v) \). Lateral extension is opposed by the relatively unstrained matrix outside the locally impacted region, causing an opposing tensile stress to be...
Enhanced dissolution of minerals: stored energy, amorphism and mechanical activation

As particle size decreases and approaches the micron to sub-micron range where mechanical activation phenomena have been reported (Báth, 2000), the required $\sigma$ reaches a very large value because of the accompanying small flaw size (e.g., a penny-shaped flaw in a 1 µm diameter particle must have $a < 0.5$ µm). The necessary impact stress $\sigma_p$ for propagation of a penny-shaped flaw is obtained from Eqs. (3) and (4):

$$\sigma_p \approx \frac{K_{IC}}{\sqrt{\pi(a)}} = \frac{K_{IC}}{2\sqrt{\pi(a)}}$$

Equation (5) can be reset in terms of average particle diameter $D$ by expressing $a$ as a fraction ($f$) of $D$:

$$\sigma_p \approx \frac{K_{IC}}{2\sqrt{\pi(Df)}}$$

where $f$ is < 0.5.

Analyses by Maurice and Courtney (1990) indicate $\sigma_p$ reaches several GPa (e.g., 2 to 6 GPa) in attrition mills. Typical $K_{IC}$ and $v$ values for minerals are ~1 to 2 MPa.m$^{1/2}$ (Rummel, 1982) and ~0.25 to 0.3 (Gebrande, 1982), respectively. Combining an upper value of 6 GPa for $\sigma_p$ with 0.3 for $v$, Eq. (6) shows that $fD$ is ~0.24 µm and ~0.97 µm for $K_{IC}$ values of 1 and 2 MPa.m$^{1/2}$, respectively. Hence, a limiting $D$ of the order of 0.5 to 2 µm is reached below which further particle fracture by attrition is unlikely. However, local shear stresses $\tau$ generated by impact loading ($\tau \approx \sigma_p/2$) are still available to promote shape change via particle plasticity (dislocation generation), provided these stresses are of sufficient magnitude. This appears to be the situation in attrition mills where, $\tau$ can become so large ($\sigma_p/2$ is ~1 to ~3 GPa) that dislocation generation is likely. Supporting evidence is provided by the studies of Murr and Hiskey (1981) who used transmission electron microscopy to demonstrate that single explosively-driven shock pulses ($\sigma_p$) of 1.2 GPa increased the dislocation density of chalcopyrite (CuFeS$_2$) crystals by $10^2$ times, rising to over $10^3$ times at 18 GPa.

The preceding fundamental analysis indicates a limiting particle size in the micron to sub-micron range is reached under the high $\sigma_p$ conditions characteristic of attrition-type milling (or similar milling techniques), and that particle fracture is replaced by increased dislocation activity. The lattice strains associated with an increased number of dislocations are expected to contribute to the “stored energy” associated with finely-milled minerals and to influence the degree of disorder (non-periodicity) or amorphism in the crystal lattice. In addition, or alternatively, the increase in internal energy may promote transitions to less thermodynamically-stable crystalline phases in minerals that exhibit polymorphism.

STORED ENERGY, AMORPHISM AND POLYMORPHISM

Stored energy

The increase in molar Gibbs free energy of milled particles due to dislocations, $\Delta G_d$, is related to changes in molar enthalpy $\Delta H_d$ and molar entropy $\Delta S_d$ associated with these dislocations:

$$\Delta G_d = \Delta H_d - T\Delta S_d \approx \Delta H_d$$

where $T$ is the temperature (K).
Dislocations are essentially one dimensional (line) imperfections and calculations suggest that their entropy effect is sufficiently small (Cottrell, 1958) that \( \Delta S_d \) becomes negligible with respect to \( \Delta H_d \), as indicated in Eq. (7). The value of \( \Delta H_d \) is determined by the elastic strain energy of all the dislocations, which is composed of linear elastic strains outside the core of each dislocation and a smaller non-linear elastic component within the core. The linear elastic strain energy per unit length of dislocation, \( \varepsilon \), contained between the radius of the dislocation core \( r_c \) and an outer bounding radius \( r_b \) remote from the core is given by Eq. (8) (Cottrell, 1958):

\[
\varepsilon \approx \frac{b^2 \mu_s}{4\pi} \ln \left( \frac{r_b}{r_c} \right)
\]

where \( b \) is the Burgers vector (displacement vector) of the dislocation and \( \mu_s \) is the elastic shear modulus.

Inclusion of the dislocation core, to provide an expression for the overall strain energy \( \varepsilon_0 \) per unit length of dislocation, is obtained with sufficient accuracy by replacing \( r_c \) by \( b/4 \) in Eq. (8) (Hirth and Lothe, 1968). The practical limit to \( r_b \) will be half the average distance between neighbouring dislocations, which is determined by the dislocation density \( \rho_d \) (total length of dislocation lines per unit volume). Thus, \( r_b \approx (\rho_d)^{1/2}/2 \) and \( \varepsilon_0 \) becomes:

\[
\varepsilon_0 \approx \frac{b^2 \mu_s}{4\pi} \ln \left( \frac{2(\rho_d)^{1/2}}{b} \right)
\]

Consequently, \( \Delta H_d \) is equal to \( \rho_d \varepsilon_0 M_V \), where \( M_V \) is the molar volume of the mineral, allowing \( \Delta G_d \) to be obtained from Eqs. (7) and (9):

\[
\Delta G_d \approx \Delta H_d = (\rho_d M_V) \frac{b^2 \mu_s}{4\pi} \ln \left( \frac{2(\rho_d)^{1/2}}{b} \right)
\]

Equation (10) provides a quantitative estimate of the increase in molar chemical free energy (increase in stored energy) due to dislocations.

Values of \( M_V \), \( b \) and \( \mu_s \) for several oxide and sulphide minerals under ambient conditions (-298 K) are listed in Table 1, together with silicon. Published crystallographic data (PDF, 1995) were used to obtain \( M_V \) and \( b \), noting that \( M_V \) is the molecular weight of the mineral divided by its density. The magnitude of \( b \) represents the size of the smallest perfect dislocation capable of maintaining lattice registry (periodicity) above and below the slip plane during motion of the dislocation. The corresponding crystallographic direction of \( b \) is included in Table 1.

The value of each \( \mu_s \) in Table 1 represents an averaged value for polycrystalline aggregates. With the exception of ilmenite and chalcopyrite, they were computed from anisotropic stiffness and compliance constants for single crystals compiled by Hearmon (1979, 1984). Computations were conducted in two ways: 1) from stiffness constants assuming uniform stress in the aggregate, and b) from compliance constants assuming uniform strain in the aggregate. The two values were then averaged. The matrix and analytical procedures required for such computations are outlined by Gebrande (1982) and Wachtman (1996). The \( \mu_s \) of ilmenite (-90 GPa) was assumed to be similar to that of TiO$_2$ (94 GPa) because of chemical and structural similarities. The \( \mu_s \) of chalcopyrite (-30 GPa) was assumed to be similar to that of sphalerite (31.3 GPa) because of structural similarities between their unit cells (Wells, 1962).
TABLE 1 Properties of selected oxide and sulphide minerals at ~298K

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Formula</th>
<th>Structure</th>
<th>Dimensions</th>
<th>$b$ (nm)</th>
<th>$M_\gamma$ ($m^3$)</th>
<th>$\mu_\gamma$ (Gpa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Magnetite</td>
<td>Fe$_3$O$_4$</td>
<td>Cubic</td>
<td>0.593687</td>
<td>[110]</td>
<td>4.453 x 10^{-5}</td>
<td>91.3*</td>
</tr>
<tr>
<td>Corundum</td>
<td>Al$_2$O$_3$</td>
<td>Trigonal</td>
<td>0.4758</td>
<td>[100]</td>
<td>2.556 x 10^{-5}</td>
<td>162*</td>
</tr>
<tr>
<td>$\alpha$-Ti$_2$O$_3$</td>
<td>Ti$_2$O$_3$</td>
<td>Trigonal</td>
<td>0.5139</td>
<td>[100]</td>
<td>3.135 x 10^{-5}</td>
<td>94*</td>
</tr>
<tr>
<td>Ilmenite</td>
<td>FeTiO$_3$</td>
<td>Trigonal</td>
<td>0.5088</td>
<td>[100]</td>
<td>3.172 x 10^{-5}</td>
<td>-90*</td>
</tr>
<tr>
<td>Rutile</td>
<td>TiO$_2$</td>
<td>Tetragonal</td>
<td>0.2959</td>
<td>[001]</td>
<td>1.880 x 10^{-5}</td>
<td>112*</td>
</tr>
<tr>
<td>$\alpha$-Quartz</td>
<td>SiO$_2$</td>
<td>Trigonal</td>
<td>0.4913</td>
<td>[100]</td>
<td>2.268 x 10^{-5}</td>
<td>44.3*</td>
</tr>
<tr>
<td>Periclase</td>
<td>NiO</td>
<td>Cubic</td>
<td>0.29776</td>
<td>[110]</td>
<td>1.1241 x 10^{-5}</td>
<td>130.3*</td>
</tr>
<tr>
<td>Bunsenite</td>
<td>ZnO</td>
<td>Hexagonal</td>
<td>0.3249</td>
<td>[100]</td>
<td>1.434 x 10^{-5}</td>
<td>46.9*</td>
</tr>
<tr>
<td>Cuprite</td>
<td>Cu$_2$O</td>
<td>Cubic</td>
<td>0.42690</td>
<td>[100]</td>
<td>2.3438 x 10^{-5}</td>
<td>10.3*</td>
</tr>
<tr>
<td>Pyrite</td>
<td>FeS</td>
<td>Cubic</td>
<td>0.5417</td>
<td>[100]</td>
<td>2.3932 x 10^{-5}</td>
<td>128*</td>
</tr>
<tr>
<td>Pyrrhotite</td>
<td>Ag$_2$SbS$_3$</td>
<td>Trigonal</td>
<td>1.104</td>
<td>[100]</td>
<td>9.249 x 10^{-5}</td>
<td>13.9*</td>
</tr>
<tr>
<td>Chalcoprite</td>
<td>CuFeS$_2$</td>
<td>Tetragonal</td>
<td>0.5289</td>
<td>[100]</td>
<td>4.3902 x 10^{-5}</td>
<td>-30*</td>
</tr>
<tr>
<td>$\beta$-Molybdenite</td>
<td>MoS$_2$</td>
<td>Hexagonal</td>
<td>0.3161</td>
<td>[100]</td>
<td>3.205 x 10^{-5}</td>
<td>51.6*</td>
</tr>
<tr>
<td>Galena</td>
<td>PbS</td>
<td>Cubic</td>
<td>0.41974</td>
<td>[110]</td>
<td>3.1494 x 10^{-5}</td>
<td>31.5*</td>
</tr>
<tr>
<td>Berndite</td>
<td>SnS$_2$</td>
<td>Trigonal</td>
<td>0.3648</td>
<td>[100]</td>
<td>4.0961 x 10^{-5}</td>
<td>22.6*</td>
</tr>
<tr>
<td>Wurtzite</td>
<td>ZnS</td>
<td>Hexagonal</td>
<td>0.382</td>
<td>[100]</td>
<td>2.3824 x 10^{-5}</td>
<td>33.3*</td>
</tr>
<tr>
<td>Sphalerite</td>
<td>ZnS</td>
<td>Cubic</td>
<td>0.38226</td>
<td>[110]</td>
<td>2.3783 x 10^{-5}</td>
<td>31.3*</td>
</tr>
<tr>
<td>Greenockite</td>
<td>CdS</td>
<td>Hexagonal</td>
<td>0.414</td>
<td>[100]</td>
<td>3.0048 x 10^{-5}</td>
<td>16.9*</td>
</tr>
<tr>
<td>Silicon</td>
<td>Si</td>
<td>Cubic</td>
<td>0.3840</td>
<td>[110]</td>
<td>1.2061 x 10^{-5}</td>
<td>66.2*</td>
</tr>
</tbody>
</table>

*Hearmon (1979); **Hearmon (1984); *Estimated.

Using Eq. (10) and the data in Table 1, the effect of an increasing dislocation density on stored energy is plotted on logarithmic scales for oxide minerals in Figure 1 and sulphide minerals in Figure 2. It is clear that an increase in $\Delta G_d > 1$ kJ/mol requires a $\rho_d > 10^{15}$ m$^{-2}$. Undeformed quartz crystals have been reported to exhibit $\rho_d$ values of $\sim 10^7$ m$^{-2}$, rising to $\sim 10^{10}$ m$^{-2}$ after severe deformation (Hobbs et al. 1976). Consequently, a $\rho_d$ of $\sim 10^{16}$ m$^{-2}$ is not unexpected during extended milling of minerals. Examination of Figures 1 and 2 indicates that the resulting $\Delta G_d$ will be in the range -0.3 to 3 kJ/mol, depending on the mineral (e.g. -0.7 kJ/mol for quartz).

Values of $\rho_d > 10^{18}$ m$^{-2}$, are considered meaningless, and excluded from Figures 1 and 2, because dislocations would be so close together (< 1 nm separation) that Eqs. (9) and (10) become invalid.

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**Fig. 1** Effect of dislocation density on stored energy $\Delta G_d$ of oxide minerals.
Energy of amorphism

The development of large numbers of dislocations, and their associated strain fields, may lead to an overall decrease in long-range lattice periodicity. This may be interpreted as the formation of a metastable "amorphous phase," because line broadening and disappearance of diffraction peaks takes place on X-ray patterns after extended milling. Estimates of the chemical free energy of amorphous phases, based on structure alone, are difficult because their atom distributions are not readily described. For example, amorphous solids have varying degrees of short-range order requiring quantification in terms of atom distribution (frequency) functions, changes in local geometry and changes in local symmetry (Gaskell, 1991). An alternative thermodynamic approach, developed in the Appendix, is to assume a basic structural similarity between the metastable amorphous phase and the liquid. This approach leads to Eq. (A10), reproduced as Eq. (11) below:

$$\Delta G_{am-cr} = \left( \frac{H_F}{T_m} \right) (T_m - T)$$

where $H_F$ is the enthalpy of fusion at the melting point $T_m$, and $\Delta G_{am-cr}$ is the estimated maximum change in chemical free energy between the metastable amorphous phase and stable crystalline phase at temperature $T$.

Estimations of $\Delta G_{am-cr}$ at 298 K and 400 K are listed in Table 2 for the minerals listed in Table 1 where both $T_m$ and $H_F$ data are available (Barin and Platzki, 1995) and for which there are no polymorphous transitions between $T$ and $T_m$. Note that $H_F$ for chalcopyrite (CuFeS$_2$) is assumed to be -63 kJ/mol, based on the likelihood that it is approximately twice that of FeS, for which $H_F$ is 31.464 kJ/mol (Barin and Platzki, 1995). This follows from the fact CuFeS$_2$ has two times more atoms per mol than FeS and, therefore, twice as many bonds to break per mol upon melting. Also, $H_F$ for pyrite (FeS$_2$) is assumed to be -66 kJ/mol because its stoichiometry and crystal structure symmetry (Wells, 1962; PDF, 1995) are identical to those of vaesite (NiS$_2$), for which $H_F$ is 65.689 kJ/mol (Barin and Platzki, 1995).

If deformation induces the formation of an amorphous phase, it is reasonable to expect the accompanying increase in chemical free energy to be reached when the thermodynamic equality condition of Eq. (12) is satisfied:

$$\Delta G_{am-cr} = \Delta G_d$$
TABLE 2 Estimation of difference in chemical free energy \( (\Delta G_{am-cr})_r \) between amorphous and crystalline phases

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Formula</th>
<th>( T_r ) (K)</th>
<th>( H_r ) (kJ/mol)</th>
<th>( (\Delta G_{am-cr})_r ) at 298 K, kJ/mol</th>
<th>Equivalent ( \rho_d ) at 298 K: ( (\Delta G_{am-cr})_r ) = ( \Delta G_d )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Magnetite</td>
<td>FeO (_2)</td>
<td>1870</td>
<td>138.072</td>
<td>116.07</td>
<td>108.54</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>( \approx 8 \times 10^{17} ) m(^2)</td>
<td></td>
</tr>
<tr>
<td>Corundum</td>
<td>AlO (_2)</td>
<td>2327</td>
<td>111.085</td>
<td>96.859</td>
<td>91.99</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>( \approx 8.5 \times 10^{17} ) m(^2)</td>
<td></td>
</tr>
<tr>
<td>Ilmenite</td>
<td>FeTiO (_3)</td>
<td>1658</td>
<td>90.793</td>
<td>74.474</td>
<td>68.889</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>( \approx 9 \times 10^{17} ) m(^2)</td>
<td></td>
</tr>
<tr>
<td>Rutile</td>
<td>TiO (_2)</td>
<td>2130</td>
<td>66.944</td>
<td>57.578</td>
<td>54.372</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Equality not reached. (^\dagger)</td>
<td></td>
</tr>
<tr>
<td>Periclase</td>
<td>MgO</td>
<td>3105</td>
<td>77.822</td>
<td>70.353</td>
<td>67.797</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>( \approx 8.8 \times 10^{17} ) m(^2)</td>
<td></td>
</tr>
<tr>
<td>Bunsenite</td>
<td>NiO</td>
<td>2228</td>
<td>54.393</td>
<td>47.117</td>
<td>44.627</td>
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<tr>
<td></td>
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<td></td>
<td></td>
<td>( \approx 8.8 \times 10^{17} ) m(^2)</td>
<td></td>
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<tr>
<td>Zincite</td>
<td>ZnO</td>
<td>2248</td>
<td>54.392</td>
<td>47.182</td>
<td>44.714</td>
</tr>
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<td></td>
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<td>Equality not reached. (^\dagger)</td>
<td></td>
</tr>
<tr>
<td>Cuprite</td>
<td>Cu(_2)O</td>
<td>1516.7</td>
<td>64.768</td>
<td>52.042</td>
<td>47.687</td>
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<td>Equality not reached. (^\dagger)</td>
<td></td>
</tr>
<tr>
<td>Pyrite</td>
<td>FeS(_2)</td>
<td>1440 (^\dagger)</td>
<td>-63*</td>
<td>52.34</td>
<td>47.67</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>( \approx 4.5 \times 10^{17} ) m(^2)</td>
<td></td>
</tr>
<tr>
<td>Chalcopyrite</td>
<td>CuFeS(_2)</td>
<td>1223 (^\dagger)</td>
<td>-63*</td>
<td>47.65</td>
<td>42.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>( \approx 1.4 \times 10^{18} ) m(^2)</td>
<td></td>
</tr>
<tr>
<td>Galena</td>
<td>PbS</td>
<td>1386.5</td>
<td>18.83</td>
<td>14.783</td>
<td>13.398</td>
</tr>
<tr>
<td></td>
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<td></td>
<td></td>
<td>( \approx 5.8 \times 10^{17} ) m(^2)</td>
<td></td>
</tr>
<tr>
<td>Wurtzite</td>
<td>ZnS</td>
<td>1995</td>
<td>10.878</td>
<td>9.2531</td>
<td>8.6969</td>
</tr>
<tr>
<td></td>
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<td></td>
<td></td>
<td>( \approx 5 \times 10^{17} ) m(^2)</td>
<td></td>
</tr>
<tr>
<td>Silicon</td>
<td>Si</td>
<td>1685</td>
<td>50.208</td>
<td>41.328</td>
<td>38.289</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Equality not reached. (^\dagger)</td>
<td></td>
</tr>
</tbody>
</table>

\(^\dagger\) Barin and Platzki (1995); \(^\dagger\) Roine (1999); \(^*\) Estimated; \(^*\) Not reached at \( \rho_d \approx 10^{18} \) m\(^2\).

Comparison of Table 1 with Figures 1 and 2 indicates satisfaction of Eq. (12) requires \( \rho_d \) to be in excess of \( 10^{17} \) m\(^2\). This is evident by examining the required \( \rho_d \) at 298 K in the last column of Table 1. In some cases, such as cuprite, zincite, rutile and silicon the equality condition is not reached at \( \rho_d \approx 10^{18} \) m\(^2\), above which Eq. (10) becomes invalid for estimating \( \Delta G_d \), indicating that complete transformation to an amorphous phase by deformation is not possible.

Note that Eq. (12) specifies the condition for which the whole mineral becomes amorphous. Thermodynamically, it does not preclude the possibility that a corresponding mol fraction of mineral is transformed to the metastable amorphous phase when \( \Delta G_d < (\Delta G_{am-cr})_r \). For example, when \( \rho_d = 10^{17} \) m\(^2\), \( \Delta G_d \) for rutile is \( \approx 4.5 \) kJ/mol. From Table 2, this corresponds to \( 7.8\% \) of \( (\Delta G_{am-cr})_r \) at 298 K, equivalent to the formation of \( \approx 8 \) mol% amorphous phase. Similarly for zincite, when \( \rho_d = 10^{17} \) m\(^2\), \( \Delta G_d \) is \( \approx 1.68 \) kJ/mol, and corresponds to formation of \( \approx 3.6 \) mol% of amorphous phase.

Energy differences associated with polymorphous transitions

Many minerals exhibit \( n \) polymorphous transitions \((n \geq 1)\), with each transition having a characteristic transition enthalpy \( (H_{3n})_h \) and transition temperature \( (T_{3n})_h \). Three minerals in Table 1, \( \alpha\)-TiO \(_2\) \((n = 1)\), \( \alpha\)-quartz \((n = 2)\) and sphalerite \((n = 2)\), exhibit such transitions. Their \((H_{3n})_h \) and \((T_{3n})_h \) are listed in Table 3. A general method to estimate differences in molar chemical free energy \( (\Delta G_{am-cr})_r \) between the metastable \((n + 1)\)th polymorph and the 1\(^{st}\) (most stable) polymorph when both are present at \( T < (T_{3n})_h \) is developed in the Appendix, leading to Eqs. (A11) and (A12). Also, a method to estimate differences in the molar chemical free energy \( (\Delta G_{am-cr})_r \) between the metastable amorphous phase and the 1\(^{st}\) polymorph when both are present at \( T < (T_{3n})_h \) is presented in the Appendix, leading to Eq. (A13). Results of calculations for \( \alpha\)-TiO \(_2\), \( \alpha\)-quartz and sphalerite, based on Eqs. (A11) to (A13), are listed in Table 3 for \( T = 298 \) K.

Following similar arguments leading to Eq. (12), it is reasonable to anticipate that deformation-induced formation of a metastable polymorphous phase is a likely occurrence at \( T < (T_{3n})_h \) when the thermodynamic equality condition of Eq. (13) is satisfied:

\[
(\Delta G_{am-cr})_T = \Delta G_d
\]
Also, similar to Eq. (12), deformation-induced formation of the amorphous phase at $T < (T_c)_{n-1}$ is expected to occur when the equality condition of Eq. (14) is satisfied:

$$\Delta G_{(n-1)} = \Delta G_d$$

(14)

Calculations of $\Delta G_{(n+1)}$ and $\Delta G_{am-1}$, based on Eqs. (A12) and (A13) respectively, are listed in Table 3. Comparison with Figures 1 and 2, and Eq. (10), indicates deformation-induced polymorphic transitions occur at lower $\rho_d$ than those necessary for formation of amorphous phases. For example, complete transformation of $\alpha$-Ti$_2$O$_3$ to $\beta$-Ti$_2$O$_3$ at 298 K requires $\rho_d = 1.5 \times 10^{15}$ m$^{-2}$, whereas formation of the amorphous phase requires $\rho_d \approx 1 \times 10^{15}$ m$^{-2}$. The latter $\rho_d$ is unrealistic and indicates that complete transformation to the amorphous phase is not possible during deformation. Similarly, transformation of sphalerite to wurtzite requires $\rho_d = 6.1 \times 10^{15}$ m$^{-2}$ and complete formation of the amorphous phase in sphalerite requires an unrealistically high $\rho_d \approx 1.6 \times 10^{18}$ m$^{-2}$. In the case of quartz, transformation of $\alpha$ to $\beta$-quartz occurs at $\rho_d = 6.3 \times 10^{15}$ m$^{-2}$, with transformation from $\alpha$-quartz to cristobalite occurring at $\rho_d = 2.3 \times 10^{16}$ m$^{-2}$ followed by transformation of $\alpha$-quartz to the amorphous phase at $\rho_d \approx 2.5 \times 10^{17}$ m$^{-2}$. Thus, the analyses suggest deformation-induced polymorphous phases are likely to be more prevalent than amorphous phases during milling of polymorphous minerals, probably forming as stacking-type faults in the crystal lattice.

**TABLE 3 Estimation of difference in chemical free energy between $(n + 1)$th and first polymorph, $(\Delta G_{(n+1)} - \Delta G_{1})_T$, and between amorphous phase and first polymorph, $(\Delta G_{am-1})_T$**

<table>
<thead>
<tr>
<th>Formula</th>
<th>1$^{st}$ Polymorph</th>
<th>$n$</th>
<th>$(n+1)^{th}$ Polymorph</th>
<th>$\Delta H_{(n)}$ (kJ/mol)$^1$</th>
<th>$T = 298$ K</th>
<th>$\Delta G_{(n+1)}$ (kJ/mol)$^1$</th>
<th>$T = 298$ K</th>
<th>$\Delta H_{m}$ (kJ/mol)$^1$</th>
<th>$T = 298$ K</th>
<th>$\Delta G_{am-1}$ (kJ/mol)$^1$</th>
<th>$T = 298$ K</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti$_2$O$_3$</td>
<td>$\alpha$-Ti$_2$O$_3$</td>
<td>1</td>
<td>$\beta$-Ti$_2$O$_3$</td>
<td>1.138</td>
<td>470</td>
<td>0.4165</td>
<td>104.6</td>
<td>2115</td>
<td>90.23</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>$\alpha$-Quartz</td>
<td>1</td>
<td>$\beta$-Quartz</td>
<td>0.728</td>
<td>847</td>
<td>0.4719</td>
<td>9.566</td>
<td>1996</td>
<td>10.054</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>2</td>
<td>Cristobalite</td>
<td>1.996</td>
<td>1079</td>
<td>1.4447</td>
<td>9.566</td>
<td>1996</td>
<td>10.054</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^1$Barin and Platzki (1995)

**CHANGES IN ACTIVATION ENERGY OF DISSOLUTION**

Principal factors governing the dissolution (leaching) of minerals under conditions where the rate controlling process is transfer of partially solvated species across the aqueous double layer have been discussed in detail previously (Tromans and Meech 1999). Figure 3(a) depicts such a situation for dissolution of an undeformed (unmilled) mineral where the molar chemical free energy of the dissolved (fully solvated) mineral species at the solvation plane is lower than in the mineral surface. As a dissolving species moves across the double layer there is an initial increase in chemical free energy, rising to a peak as it becomes a partially solvated activated complex, then decreasing as it approaches and becomes fully solvated at the solvation plane. The activation energy for dissolution (forward direction) is denoted $\overrightarrow{\Delta G}$, and that for deposition (reverse direction) is $\overleftarrow{\Delta G}$, where $\overrightarrow{\Delta G} < \overleftarrow{\Delta G}$. Based on Arrhenius rate law behaviour, the resulting dissolution rate $R_1$ (mol.m$^{-2}$.s$^{-1}$) is given by Eq. (15),

$$R_1 = \overrightarrow{R} - \overleftarrow{R} = A[\exp(-\overrightarrow{\Delta G}/RT) - \exp(-\overleftarrow{\Delta G}/RT)]$$

(15)

where $\overrightarrow{R}$ and $\overleftarrow{R}$ are rates in the dissolution and deposition directions, respectively, $A$ is a rate constant (mol.m$^{-2}$.s$^{-1}$), and $R$ is the gas constant (8.3144 J.K$^{-1}$.mol$^{-1}$).
The second exponential term in Eq. (15) is negligible with respect to the first during normal milling practice (Tromans and Meech, 1999), so that Eq (15) becomes:

\[ R, \approx R \approx A \exp(-\Delta G_1 / RT) \]  

(16)

The dissolution of a deformed (milled) mineral with stored energy \( \Delta G_d \) is depicted in Figure 3(b). The molar activation energy of dissolution is decreased from \( \Delta G_1 \) to \( \Delta G_2 \), whereas the peak energy of the activated complex and \( \Delta G \) remain unchanged. Thus, from Eq. (16) the dissolution rate \( R_2 \) of the deformed mineral becomes:

\[ R_2 \approx A \exp \left( -\frac{\Delta G_2}{RT} \right) = A \exp \left( \frac{\Delta G_d - \Delta G_1}{RT} \right) \]  

(17)

The resulting dissolution rate ratio \( R_2/R_1 \) is obtained from Eqs. (16) and (17):

\[ R_2 / R_1 \approx \exp(\Delta G_d / RT) \]  

(18)

Fig. 3  Schematic diagrams showing changes in activation energy of dissolution: a) Dissolution of undeformed mineral with activation energy of dissolution \( \Delta G_1 \); b) Reduced activation energy of dissolution \( \Delta G_2 \) caused by stored energy \( \Delta G_d \).

The effects of different \( \Delta G_d \), produced by milling, on dissolution rate ratios at \( T = 298 \) K and 400 K are summarised in Figure 4, where axes are scaled logarithmically. Evidently, increasing \( T \) decreases \( R_2/R_1 \) and an increase in chemical free energy of dissolution \( \Delta G_d \approx 0.3 \) kJ/mol has insignificant effect (~10–13% increase) on the rate ratio. A threefold rate increase requires a \( \Delta G_d \) of ~3.0 kJ/mol, corresponding to very high \( \rho_d > 10^{16} \) m\(^{-2}\) in both oxide and sulphide minerals (see Figures 1 and 2). Rate increases >> 50 times are indicated if \( \Delta G_d \) is > 10 kJ/mol. However, such high dissolution rates may never be achievable in practice, because
subsequent mass transfer controlled processes in the liquid phase will limit the rate of transport of reactants
to the mineral surface and/or transport of dissolved products from the surface.

Note that the effects of $\Delta G_d$ on dissolution rates may be discussed equally in terms of increased
dislocation density or generation of metastable polymorphous and/or amorphous phases, provided the
equality conditions of Eqs. (12) to (14) are satisfied. Again, achievable rate increases will be subject to
mass transfer limitations so that minerals containing amorphous phase (equivalent to a $\Delta G_d = (\Delta G_{am})_f$
with $\rho_d$ approaching $10^{18}$ m$^{-2}$ in Table 2) may not dissolve any faster than milled minerals having lower
$\Delta G_d$ (lower $\rho_d$) and no amorphous phase.

![Fig. 4 Effect of change in stored energy $\Delta G_d$ on dissolution rate ratio $R_2/R_1$ at 298 K and 400 K.](image)

A situation of more likely interest in mineral processing is comparison of the dissolution rate $R_1$ of milled
particles having an average stored energy of $(\Delta G_d)_1$ with the dissolution rate $R_2$ of milled particles having
a higher $(\Delta G_d)_2$ due to different milling conditions. In this case, the rate ratio $R_2/R_1$ is a modified form of
Eq. (18):

$$R_2/R_1 \approx \exp \left[ \frac{(\Delta G_d)_2 - (\Delta G_d)_1}{RT} \right]$$

### COMPARISON WITH MECHANICAL ACTIVATION PHENOMENA

**Structural changes**

Few direct observations have been made of crystal defects and structural transformations produced by
extended milling. One relevant study by Shen et al. (1995) was conducted on shaker-milled Si powders
using high-resolution transmission electron microscopy. They observed formation of amorphous regions
occupying an average ~15% by volume. At 298 K, 15% of $(\Delta G_{am})_f$ for Si corresponds to 6.2 kJ/mol (see
Table 2), suggesting this was the average $\Delta G_d$, for which the equivalent $\rho_d$ was near $2.9 \times 10^{17}$ m$^{-2}$ (see
Eq. (10) and data in Table 1). The average spacing between dislocations calculated from $(\rho_d)^{-1/2}$ is ~2 nm.
The crystallite size in amorphous-free regions of the Si particles was ~3 nm. This is close to, and consistent
with the calculated dislocation spacing of 2 nm based on the fraction of amorphous phase.

Tkáčová et al. (1993) used X-ray diffraction to measure structural changes related to disorder (loss of
periodicity) in a mixed sulphide concentrate during extended milling. Disorder was analysed via changes in
Enhanced dissolution of minerals: stored energy, amorphism and mechanical activation

The shape and intensity of X-ray peaks, from which they inferred the percentage of amorphous phase. The concentrate contained chalcopyrite, sphalerite and galena minerals. Their results indicated a limiting percentage of amorphous phase was approached during milling, increasing in the order chalcopyrite (50%) < galena (65%) < sphalerite (70%). Such behaviour may be explained in terms of the deformation behaviour of different minerals. As dislocations are generated and move under the shear stress \( \tau \) produced by impact stresses \( \tau_p \) on the particles (maximum \( \tau = \tau_p/2 \)), \( \rho_d \) increases and causes work hardening. Eventually, further particle deformation becomes negligibly small as work hardening raises the yield stress \( \tau_y \) to \( \tau_p/2 \). Under these circumstances, Eq. (20) is an approximate description of the resulting situation for small particles:

\[
\tau_y \approx \tau_0 + \alpha_\mu b (\rho_d)^{1/2} \approx \tau_p/2
\]

(20)

where \( \tau_0 \) is the lattice friction stress (Peierls stress) opposing dislocation slip (Hirth and Lothe, 1968) and \( \alpha_\mu \) is a constant of the order of 0.1 (Cottrell, 1958).

By rearranging Eq. (20) an expression can be obtained for \( \rho_d \) as follows:

\[
\rho_d = \left( \frac{\tau_p - 2\tau_0}{2\alpha_\mu b} \right)^2
\]

(21)

All sulphide particles in the mixed concentrate studied by Tkáčová et al. (1993) were subject to the same milling conditions and experienced the same maximum \( \tau_p \), as high as \(-6 \) GPa in attrition mills (Maurice and Courtney, 1990). Since \( \tau_0 \approx 0.1 \mu_s \) for covalent crystals and less for other types (Hirth and Lothe, 1968), this suggests an upper \( \tau_p \) value of \(-0.3 \) GPa for sphalerite, chalcopyrite and galena (see Table 1). Hence, \( \tau_0 \) is negligible relative to \( \tau_p \) in Eq. (21) so that differences in \( \rho_d \) for each milled sulphide are directly related to the product \( (\mu_s b)^2 \). Lattice disorder arises from an increase in \( \rho_d \) which, in turn, is influenced by \( (\mu_s b)^2 \). Referring to the data in Table 1, \( (\mu_s b)^2 \) is calculated as \( 5.765 \times 10^{-11} \), \( 10.161 \times 10^{-11} \) and \( 18.046 \times 10^{-11} \) Pa\(^{-2}\)m\(^2\) for chalcopyrite, galena and sphalerite, respectively; the same order in which an increase in the limiting disorder (amorphism) was observed in the mixed concentrate.

Enhanced dissolution effects

The effect of \( \Delta G_d \) on enhanced dissolution (leaching) rates of minerals is realised only when chemical dissolution is controlled at the surface by transfer of partially solvated complexes across the double layer. There will be little or no influence under conditions where a solid reaction product film (passivating layer) forms on the mineral surface or where dissolution is controlled by mass transport in the liquid phase, the latter situation being typified by an activation energy of \(-17 \) kJ/mol (Tromans and Meech, 1999).

Oxidative leaching of chalcopyrite (CuFeS\(_2\)) is an example of a system where passivation effects may occur, usually attributed to sulphur films and/or intermediate decomposition products of the mineral (Jones and Peters, 1976; Murr and Hiskey, 1981; Yin et al., 2000). However, Murr and Hiskey (1981) have reported on the leaching of chalcopyrite in a sulphuric acid/dichromate solution at 323 K wherein no passivation was observed and an activation energy of 50 kJ/mol was measured: a characteristic of chemically controlled dissolution. Moreover, they compared dissolution rates of mineral fractions obtained from chalcopyrite milled from natural state crystals (\( \rho_d \approx 10^{15} \) m\(^{-2}\)) with similar size fractions milled from crystals shock-loaded at \(-18 \) GPa (\( \rho_d \approx 10^{15} \) m\(^{-2}\)), where \( \rho_d \) was determined by conventional transmission electron microscopy (CTEM). Final particle fractions were \(-48-65 \) mesh (250-210 \( \mu \)m) and \(-100-150 \) mesh (125-100 \( \mu \)m), which, from Eqs. (5) and (6), were sufficiently large that particle fracture only, with no deformation, was expected during milling. Hence, if \( \rho_d \) remained unchanged throughout milling, the shock-loaded and milled material (initial \( \rho_d \approx 10^{15} \) m\(^{-2}\)) ought to exhibit a higher dissolution rate than
crystals milled in the natural state (initial \( \rho_d \sim 10^{11} \text{ m}^{-2} \)). Such anticipated behaviour was observed, dissolution being 1.5 to 2 times higher for crystals milled after shock loading at 18 GPa relative to milled natural crystals. However, the rate ratio was significantly higher than that predicted (~1.05) from Eqs. (10) and (19). A possible explanation for this discrepancy is that \( \rho_d \) for the shock loaded crystals was larger than \( \sim 10^{15} \text{ m}^{-2} \) reported by Murr and Hiskey (1981). Examination of the published CTEM micrograph of their shock-loaded crystal shows regions where dislocation images are so close together as to be indistinguishable from each other. The CTEM image of a single dislocation usually has a width of 10 nm (strain field effects). Hence if dislocations are so close as to be indistinguishable, their separation is \( \sim 10 \text{ nm} \) (or less), corresponding to a \( \rho_d \) of at least \( \sim 10^{16} \text{ m}^{-2} \). Under these circumstances Eqs.(10) and (19) predict a higher dissolution rate ratio of ~1.5, consistent with the observations.

Welham and Llewellyn (1998) reported increased leaching rates of ilmenite in sulphuric acid after extended milling. The activation energy of dissolution was reduced from within the range ~70 to ~80 kJ/mol (slow chemical dissolution control) to near ~15 kJ/mol (faster mass transport control) and corresponded to an overall decrease in activation energy of ~60 kJ/mol. From the data for ilmenite in Figure 1, this activation energy decrease (equivalent to a required \( \Delta G_d \) of ~60 kJ/mol) is readily achieved with a \( \rho_d \) of 7 x 10^{17} \text{ m}^{-2} or, from Table 2, by formation of an amorphous phase where \( (\Delta G_{am-cr})_T \) is ~70 kJ/mol.

**Microtopography and stored energy**

Previous theoretical work has shown that surface microtopography significantly influences the dissolution of particles in the micron to sub-micron range (Tromans and Meech, 1999). The activation energy of dissolution from surface sites at the edges of steps was estimated to be approximately ~20% less than dissolution from surface sites at terraces, leading to a higher dissolution rate at steps. A high density of surface steps arising from particle fracture and cleavage during milling supplies a surface with a large fraction of step sites, leading to an overall increase in the rate of particle dissolution. When deformation-induced stored energy \( \Delta G_d \) is present, the activation energy for dissolution is also reduced, as shown in Figure 3b and Eq. (17). This reduction applies to all types of dissolution sites, including steps and terraces. Thus, stored energy and microtopography act in synergy to promote enhanced mineral dissolution when both effects are present.

**CONCLUSIONS**

Theoretical analyses of fine particle behaviour with particular reference to oxide and sulphide minerals, lead to the following conclusions:

1. A limiting particle size in the micron to sub-micron range is reached during extended grinding with attrition-type mills, after which particle fracture is replaced by particle deformation. This limiting particle size is controlled by the fracture toughness of the mineral and the impact loading stresses.

2. Deformation-induced changes in the dislocation density of minerals are quantitatively related to an increase in stored energy. Dislocation densities of \( \sim 10^{16} \text{ m}^{-2} \) are required to produce a stored energy of ~0.3 to ~3 kJ/mol, depending on the mineral.

3. A deformation-induced amorphous phase produces an increase in stored energy ranging from ~10 to ~100 kJ/mol at 298 K, depending on the mineral. This increase is equivalent to energy changes produced by dislocation densities in excess of \( 10^{17} \text{ m}^{-2} \).

4. Stored energy associated with a deformation-induced polymorphous phase is much lower than for an amorphous phase.
Thermodynamically, stored energy effects may be considered either in terms of lattice disorder related to dislocation density and/or that due to the production of a particular fraction of amorphous (and polymorphous) phase.

The activation energy of dissolution is decreased by an amount directly related to the change in stored energy when dissolution is controlled by transfer of partially solvated species across the aqueous double layers. The resulting effect is an increased dissolution rate (mechanically-activated dissolution). A stored energy increase of ~3 kJ/mol produces a threefold increase in dissolution rate at 298 K.

**APPENDIX**

**Estimated chemical free energy of amorphous phase \( G_{am} \)**

The amorphous phase is thermodynamically unstable, relative to the crystalline phase, and estimation of its free energy is based upon the hypothetical behaviour of the amorphous phase if it could be preserved below and up to the melting point. Calculation procedures utilise absolute values of the standard state molar values of the Gibbs free energy (\( G \)), enthalpy (\( H \)) and entropy (\( S \)) of single species (see Barin and Platzki, 1995), where subscripts \( am, cr \) and \( liq \) denote amorphous, crystalline and liquid phases, respectively.

Estimation of the maximum value of \( G_{am} \) is based on the following conditions:

1. The amorphous phase is treated as a glass-type solid where the atom disorder is similar to that of the liquid phase, except that the atom positions are fixed (apart from thermal vibrations) and unable to undergo long range diffusion movements characteristic of liquids.

2. The \( T \)-dependent variations of the molar heat capacities \( C_p \) of the corresponding amorphous and crystalline solids are assumed to be similar. This follows from condition 1 and is supported by observed similarities in \( C_p \) behaviour between corresponding crystalline and amorphous glass phases in glass-forming minerals, e.g., anorthite, diopside, amphibole and quartz in Figure A1. The \( C_p \) data were obtained from Perry et al. (1984).

3. At all \( T \), \( S_{am} > S_{cr} \). This is consistent with the general concept that the entropy of a disordered solid phase must always be larger than its crystalline counterpart.

4. The value of \( S_{am} \) must have a finite value at 0 K. This follows from condition 3 together with the thermodynamic requirement that \( S_r \) for a perfect crystal is zero at 0 K (Barin and Platzki, 1995).

The basic thermodynamic equation for the absolute Gibbs free energy of a single species is given by Eq. (A1):

\[
G = H - TS
\]  

At the melting point of the crystal, \( T_m \), thermodynamic equilibrium requires \( (G_{am})_{T_m} = (G_{liq})_{T_m} \), leading to Eq. (A2):

\[
(G_{am})_{T_m} = (H_{am})_{T_m} - T_m(S_{am})_{T_m} = (G_{liq})_{T_m} = (H_{liq})_{T_m} - T_m(S_{liq})_{T_m} = (H_{cr})_{T_m} + H_F - T_m(S_{cr})_{T_m} \]  

where \( H_F \) is the molar enthalpy of fusion for the crystal/liquid phase transition and \( (H_{am})_{T_m} + H_F = (H_{liq})_{T_m} \).

From Eq. (A2), it is evident that:

\[
T_m(S_{am})_{T_m} = T_m(S_{cr})_{T_m} + H_F
\]  

After applying condition 1, which requires the entropy of the amorphous phase at $T_m$ to be the same as the liquid phase, $(S_{am})_{T_m} = (S_{liq})_{T_m}$, Eq. (A3) leads to:

$$\frac{HF}{S_{T_m}} = (S_{liq})_{T_m} + \frac{H_F}{T_m} \quad \text{(A4)}$$

The entropy of a single species at any temperature $T$ is related to that at another temperature, such as $T_m$, via Eq. (A5):

$$S_T = S_{T_m} + \int_{T_m}^T \frac{C_P}{T} \, dT \quad \text{(A5)}$$

Therefore, applying condition 2 (T-dependent variation of $C_P$ is the same for the crystalline and amorphous phases), it is obvious from Eqs. (A4) and (A5) that $(S_{am})_T > (S_{cr})_T$ at all $T$, which meets conditions 3 and 4.

The general thermodynamic relationship relating the free energy $G_T$ of a single species at temperature $T$ to the free energy $G_{T_m}$ of the species at $T_m$ is given by Eq. (A6):

$$G_T = G_{T_m} + \int_{T_m}^T C_P \, dT - (T - T_m)S_{T_m} - T_m \int_{T_m}^T \frac{C_P}{T} \, dT \quad \text{(A6)}$$

Applying Eq. (A6) to the amorphous and crystalline phases at $T$ and $T_m$, where $T < T_m$, leads to Eqs. (A7) and (A8):

$$G_{T} = G_{T_m} + \int_{T_m}^T C_P \, dT - (T - T_m)(S_{T_m})_T - T_m \int_{T_m}^T \frac{C_P}{T} \, dT \quad \text{(A7)}$$
(G_{am})_T = (G_{am})_{T_m} + \int_{T_m}^{T} C_p \delta T - (T - T_m)(S_{am})_{T_m} - T \int_{T_m}^{T} \frac{C_p}{T} \delta T \quad (A8)

Thermodynamic equilibrium at $T_m$ requires $(G_{cr})_{T_m} = (G_{aq})_{T_m} = (G_{am})_{T_m}$. Thus, after applying condition 2 relating to similarity of $C_p$, subtraction of Eq. (A7) from (A8) yields (A9):

$$(G_{am})_T - (G_{cr})_T = (\Delta G_{am-cr})_T = (T_m - T)\{(S_{am})_{T_m} - (S_{cr})_{T_m}\}$$ \quad (A9)

where $(\Delta G_{am-cr})_T$ is the difference in molar free energy between the amorphous and crystalline solids at temperature $T$.

Inserting Eq. (A4) into Eq. (A9) leads to the estimated value of $(\Delta G_{am-cr})_T$:

$$(\Delta G_{am-cr})_T = \left(\frac{H_f}{T_m}\right)(T_m - T)$$ \quad (A10)

from which $(G_{am})_T$ is readily calculated from known values of $(G_{cr})_T$.

**Estimated chemical free energy difference between polymorphous phases**

Many minerals exhibit polymorphous phases having identical chemical stoichiometry and different crystal structures (e.g. the wurtzite and sphalerite polymorphs of ZnS in Table 1). Similar to solid-liquid transformations, there is an equilibrium transition temperature $T_\alpha$ below which one polymorph (phase 1) is most thermodynamically stable and above which the other (phase 2) is most stable. If both polymorphs are present at $T < T_\alpha$, there will be a difference in molar chemical free energies $(\Delta G_{2\rightarrow 1})_T$ between the phases at $T$. If the temperature-dependent behaviour of $C_p$ is closely identical in both phases, analogous arguments to those leading to Eq. (A10) may be applied to $(\Delta G_{2\rightarrow 1})_T$ to produce Eq. (A11):

$$(\Delta G_{2\rightarrow 1})_T = \left(\frac{H_\alpha}{T_\alpha}\right)(T_\alpha - T)$$ \quad (A11)

where $H_\alpha$ is the enthalpy of transition from phase 1 to phase 2 at $T_\alpha$.

The validity of Eq. (A11) may be tested by examining the thermodynamic behaviour of sphalerite and wurtzite polymorphs of ZnS, where $T_\alpha = 1293$ K and $H_\alpha = 13,024$ kJ/mol (Barin and Platzki, 1995). Sphalerite is the most stable phase below $T_\alpha$. However, both phases may be present at $T < T_\alpha$. The $T$-dependent $C_p$ data reported by Barin and Platzki (1995), shown in Figure A2, confirm that both polymorphs exhibit almost identical $C_p$ behaviours, as required for Eq. (A11). After inserting $T_\alpha$ and $H_\alpha$ values for ZnS into Eq. (A11), and denoting sphalerite as phase 1 and wurtzite as phase 2, $(\Delta G_{2\rightarrow 1})_T$ is 10.022 kJ/mol at $T = 298$ K, and 8.995 kJ/mol at 400 K. Absolute values of $G$ listed by Barin and Platzki (1995) for sphalerite $(G_{sp})$ are $-222.373$ and $-228.975$ kJ/mol at 298 K and 400 K, respectively. Corresponding $G$ values for wurtzite $(G_w)$ are $-212.107$ and $-219.678$ at 298 K and 400 K, respectively. Subtraction of $G_{sp}$ from $G_w$ yields $(\Delta G_{2\rightarrow 1})_T$ values of 10.266 kJ/mol at 298 K, and 9.297 kJ/mol at 400 K, which are within 2.38% and 3.25% respectively of the estimates obtained from Eq. (A11).
If $n$ polymorphous transitions occur with increasing $T$, consistent with $n + 1$ polymorphs, Eq. (A11) may be written in a more general form:

$$\left(\Delta G_{(n+1)}\right)_T = \sum_{n=1}^{n=n} \left(\frac{H_n}{T_n}\right) \left[(T_n) - T\right]$$  \hspace{1cm} (A12)

where $(H_n)_{_T}$ is the enthalpy of the $n$th polymorphous transition at temperature $(T_n)_{_T}$, $(\Delta G_{(n+1)})_{_T}$ is the difference in chemical free energy between the $(n + 1)$th and first polymorph, and $T$ is below the first transition temperature (i.e. $T < (T_n)_{_{n-1}}$).

Note that when $n$ allotrope transitions occur with increasing $T$, $H_F$ corresponds to the enthalpy of fusion for the $(n + 1)$th polymorph. Consequently, the estimated difference in chemical free energy $(\Delta G_{am-1})_T$ between the amorphous phase and first polymorph at $T < (T_n)_{_{n-1}}$ is obtained from a combination of Eqs. (A10) and (A12):

$$\left(\Delta G_{am-1}\right)_T = \sum_{n=1}^{n=n} \left(\frac{H_n}{T_n}\right) \left[(T_n) - T\right] + \left(\frac{H_F}{T_m}\right) (T_m - T)$$  \hspace{1cm} (A13)

### LIST OF SYMBOLS

- $A$ Rate constant (mol.m$^{-2}$.s$^{-1}$).
- $C_p$ Molar heat capacity (J.mol$^{-1}$.K$^{-1}$).
- $D$ Average particle diameter (m).
- $E$ Tensile elastic modulus (Pa).
- $G$ Standard (absolute) chemical free energy of single species (J/mol).
- $G_{am}$, $G_{cr}$, $G_{liq}$ $G$ for amorphous, crystalline and liquid phase, respectively (J/mol).
- $G_{sc}$ Critical strain energy release rate at fracture (J/m$^2$).
- $H$ Standard (absolute) enthalpy of single species (J/mol).
- $H_{am}$, $H_{cr}$, $H_{liq}$ $H$ for amorphous, crystalline and liquid phase, respectively (J/mol).
- $H_F$ Enthalpy of fusion (J/mol).
- $H_n$ Enthalpy of polymorphous phase transition at $T_n$ (J/mol).
- $(H_n)_{n}$ Enthalpy of $n$th polymorphous phase transition at $(T_n)_{n}$ (J/mol).
Enhanced dissolution of minerals: stored energy, amorphism and mechanical activation

\[ K_{ic} \] Critical stress intensity at particle fracture (Pa.m^{1/2}).

\[ M_v \] Molar volume (m^3).

\[ R \] Gas constant (8.3144 J.K^{-1}.mol^{-1}).

\[ R_1 \] Resulting dissolution rate with activation energy (mol.m^{-2}.s^{-1}).

\[ R_2 \] Resulting dissolution rate with activation energy \( \Delta G_2 \) (mol.m^{-2}.s^{-1}).

\[ R_{s} \] Resulting dissolution rate with stored energy \( \Delta G_{s} \) (mol.m^{-2}.s^{-1}).

\[ R_{t} \] Resulting dissolution rate with stored energy \( \Delta G_{t} \) (mol.m^{-2}.s^{-1}).

\[ \bar{R} \] Reverse rate (deposition, mol.m^{-2}.s^{-1}).

\[ \bar{S} \] Standard (absolute) entropy of single species (J.mol^{-1}.K^{-1}).

\[ S_{am}, S_{cr}, S_{liq} \] S for amorphous, crystalline and liquid phase, respectively (J.mol^{-1}.K^{-1}).

\[ T \] Temperature (K).

\[ T_{m} \] Temperature at melting (fusion) point (K).

\[ T_{e}\alpha \] Equilibrium temperature of polymorphous phase transition (K).

\[ T_{e}\alpha \] Equilibrium temperature of \( \alpha \)th polymorphous phase transition (K).

\[ Y \] Geometrical factor related to crack shape.

\[ \Delta G \] Free energy difference (J/mol).

\[ \Delta G_{d} \] Increase in molar free energy (stored energy) due to dislocations (J/mol).

\[ \Delta G_{(d)} \] Increase in \( \Delta G_{d} \) for condition 1 (J/mol).

\[ \Delta G_{(d)} \] Increase in \( \Delta G_{d} \) for condition 2 (J/mol).

\[ \Delta G_{(am-cr)} \] \( \Delta G \) between amorphous and crystal phase at T (J/mol).

\[ \Delta G_{(2-1)} \] \( \Delta G \) between polymorphous phases 2 and 1 at T (J/mol).

\[ \Delta G_{(n+1)-1} \] \( \Delta G \) between \( (n+1) \)th and first polymorphous phase at T (J/mol).

\[ \Delta G_{1} \] Activation energy for dissolution (forward direction, J/mol).

\[ \Delta G_{2} \] Activation energy for dissolution with stored energy \( \Delta G_{d} \) (J/mol).

\[ \Delta H \] Enthalpy increase due to dislocations (J/mol).

\[ \Delta S \] Entropy increase due to dislocations (J.mol^{-1}.K^{-1}).

\[ a \] Flaw size (m).

\[ b \] Burgers vector of dislocation (m).

\[ f \] A fraction < 0.5.

\[ n \] Number of polymorphous transitions.

\[ r \] Outer bounding limit (radius) of strain field around a dislocation (m).

\[ r_c \] Radius of dislocation core.

**Greek symbols**

\[ \alpha, \] A constant with an approximate value of 0.1.

\[ \varepsilon \] Strain energy per unit length of dislocation excluding core energy (J/m).

\[ \varepsilon_{ul} \] Strain energy per unit length of dislocation including core energy (J/m).

\[ \gamma \] Surface free energy (J/m^2).

\[ \mu_s \] Elastic shear modulus (Pa).

\[ \nu \] Poisson's ratio.

\[ \rho_d \] Dislocation density (m^{-2}).

\[ \sigma_c \] Critical tensile stress for fracture (Pa).

\[ \sigma_m \] Maximum impact stress (Pa).

\[ \tau \] Shear stress (Pa).

\[ \tau_{li} \] Lattice friction stress (Pa).

\[ \tau_c \] Shear stress at yielding (Pa).
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