Surface properties and dissolution of mineral fibres

Pacella A.

Dipartimento di Scienze della Terra, Sapienza Università di Roma, Piazzale Aldo Moro 5, 00185 Roma, Italy
Why do we need to study fibre dissolution?

- Dissolution rates of mineral fibres are used as a proxy of their biodurability (i.e. the ability to resist to chemical/biochemical alteration).

- Although dissolution experiments do not reproduce the complexity of processes that can occur in human body, they may provide a insight on the interaction between fibres and biological environment.

- Investigation of the dissolution mechanism of fibres is the key to understand the behaviour of the fibres during weathering.
The fibre dissolution experiments: the \textit{in vitro} tests

- \textbf{cellular \textit{in vitro} investigation} includes the treatment of cultured cells (usually alveolar macrophages) with fibers, followed by microscopic examination of the intracellular fibers to determine the change in their diameter and composition.

- \textbf{acellular \textit{in vitro} investigation} includes leaching of the fibres into dissolution media.
The dissolution media

- Inorganic buffered solutions
- Simulated biological fluids
The dissolution media

Inorganic buffered solutions

- pH < 5 (i.e. alveolar macrophages pH 4.5, acidic rain) can be maintained by acids (HCl, HNO₃, CH₃COOH).

- Intermediate pH conditions (i.e. physiological pH 7.4, natural waters pH 6.5-8.5) can be obtained with phosphate buffer solutions (Na₂HPO₄ + NaH₂PO₄).

- pH > 9 (CO₂ sequestration processes by serpentinites) can be maintained by carbonates or Na (or K) hydroxides.
The dissolution media

Simulated biological fluids

- **Artificial lysosomal fluid (pH 4.5)** is employed to mimic the environment with which inhaled particles would come into contact after phagocytosis by alveolar and interstitial macrophages.

- **Gamble’s solution (pH 7.4)** simulates the interstitial lung fluid and airway lining fluid.

- **Gamble’s solution (pH 4.5)** simulates environment with which inhaled particles would come into contact after phagocytosis by alveolar and interstitial macrophages.
## The dissolution media

### Composition of the simulated biological fluids

<table>
<thead>
<tr>
<th>Composition</th>
<th>ALF (g/L)</th>
<th>Gamble’s solution (g/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Magnesium chloride</td>
<td>0.050</td>
<td>0.095</td>
</tr>
<tr>
<td>Sodium chloride</td>
<td>3.21</td>
<td>6.019</td>
</tr>
<tr>
<td>Potassium chloride</td>
<td>–</td>
<td>0.298</td>
</tr>
<tr>
<td>Disodium hydrogen phosphate</td>
<td>0.071</td>
<td>0.126</td>
</tr>
<tr>
<td>Sodium sulfate</td>
<td>0.039</td>
<td>0.063</td>
</tr>
<tr>
<td>Calcium chloride dihydrate</td>
<td>0.128</td>
<td>0.368</td>
</tr>
<tr>
<td>Sodium acetate</td>
<td>–</td>
<td>0.574</td>
</tr>
<tr>
<td>Sodium hydrogen carbonate</td>
<td>–</td>
<td>2.604</td>
</tr>
<tr>
<td>Sodium citrate dihydrate</td>
<td>0.077</td>
<td>0.097</td>
</tr>
<tr>
<td>Sodium hydroxide</td>
<td>6.00</td>
<td>–</td>
</tr>
<tr>
<td>Citric acid</td>
<td>20.8</td>
<td>–</td>
</tr>
<tr>
<td>Glycine</td>
<td>0.059</td>
<td>–</td>
</tr>
<tr>
<td>Sodium tartrate dihydrate</td>
<td>0.090</td>
<td>–</td>
</tr>
<tr>
<td>Sodium lactate</td>
<td>0.085</td>
<td>–</td>
</tr>
<tr>
<td>Sodium pyruvate</td>
<td>0.086</td>
<td>–</td>
</tr>
<tr>
<td>pH</td>
<td>4.5</td>
<td>7.4</td>
</tr>
</tbody>
</table>

Modified from Marques et al., 2011
Experimental

Batch reactor

Flow-through reactor

Solid:solution ratio between 2 and 10 gL\(^{-1}\)

Aliquots of the suspension are periodically withdrawn, filtered and analysed for the desired elements (Si, Al, Mg…)

Atomic absorption spectr.

Inductively coupled plasma spectr.
Experimental

Batch reactor

Inert container where a known mass of fibres is kept in contact with a fixed volume of fluid.

The ions released during mineral dissolution accumulate in the solution, whose composition evolves and may reach saturation, so that fibre dissolution could be inhibited.

Batch reactor is a closed system. It may represent some portions of the lung (e.g. fiber inside a macrophage) that behave as at least partially closed system.
Batch reactor: dissolution rate calculation

\[ \text{Rate}_j (\text{mol g}^{-1} \text{s}^{-1}) = - \frac{1}{v_j M} \left( \frac{dC_j}{dt} \right) \]

- \( v_j \) is the stoichiometric coefficient of component j
- \( V \) is the volume of solution (L)
- \( M \) is the mineral mass (g)
- \( \frac{dC_j}{dt} \) is the variation of the concentration of the component j \((C_j)\) with time (t)

Rates may be normalized to the BET surface area \((m^2 \text{g}^{-1})\)
Experimental

Flow-through reactor

The flow-through reactor is an **opened system**. It is recommendable to avoid reaching equilibrium, which may restrict dissolution, and is more representative of dissolution occurring in **biological medium**.
Flow-through reactor: dissolution rate calculation

\[
Rate_j (\text{mol g}^{-1} \text{s}^{-1}) = -\frac{1}{\nu_j M} \frac{q}{C_{j,\text{out}} - C_{j,\text{in}}}
\]

\(\nu_j\) is the stoichiometric coefficient of component \(j\).

\(M\) is the mineral mass (g).

\(q\) is the volumetric fluid flow (mL min\(^{-1}\)).

\(C_{j,\text{out}}\) and \(C_{j,\text{in}}\) are the concentrations of the \(j\) component in the output and input solutions, respectively.

Rate < 0 for dissolution \quad Rate > 0 for precipitation
The dissolution rate of silicates is generally calculated from Si concentrations ($R_{Si}$) in the output solution as it is considered as the rate-limiting step in the dissolution reaction.

In chemical kinetics the overall rate of a reaction is approximately determined by the slowest step, known as the rate-limiting step.
Flow-through reactor: dissolution rate calculation

\[ \text{Rate}_j (\text{mol g}^{-1} \text{s}^{-1}) = -\frac{1}{V_j M} \left( C_{j,\text{out}} - C_{j,\text{in}} \right) \]

The dissolution rate is calculated at steady-state.

For silicates, the steady state is assumed to prevail when the Si output concentration remained fairly constant (i.e. ±6%).

At steady-state, dissolution is expected to proceed under far-from-equilibrium conditions.
Dissolution rate calculation

Flow – through experiments

\[
Rate_j \text{ (mol g}^{-1}\text{s}^{-1}) = -\frac{1}{v_j M} (C_{j,\text{out}} - C_{j,\text{in}})
\]

Average steady state

Batch experiments

\[
Rate_j \text{ (mol g}^{-1}\text{s}^{-1}) = -\frac{1}{v_j M} \frac{dC_j}{dt}
\]

Modified from Rozalen et al. (2013)

Modified from Rozalen et al. (2008)
General form of the rate law for heterogeneous mineral surface reaction:

\[ \text{Rate} = k_0 A_{\text{min}} e^{-E_a/RT} a_{H^+}^{n_{H^+}} g(I) \prod_i a_i^{n_i} f(\Delta G_r) \]

General form of the rate low for heterogeneous mineral surface reaction

\[ \text{Rate} = k_0 A_{\text{min}} e^{-E_a/RT} a_{H^+}^{n_{H^+}} g(I) \prod_i a_i^{n_i} f(\Delta G_r) \]

\( k_0 \) is an intensive rate constant (moles/cm\(^2\)/sec) and incorporates all the pre-exponential factors involving the mineral surface dynamics.
General form of the rate law for heterogeneous mineral surface reaction

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\(A_{\text{min}}\) is the surface area of the mineral (m\(^2\)).
General form of the rate law for heterogeneous mineral surface reaction

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- \( k_0 \) is an intensive rate constant (moles/cm²/sec) and incorporates all the pre-exponential factors involving the mineral surface dynamics.

- \( A_{\text{min}} \) is the surface area of the mineral (m²).

- \( e^{-E_a/RT} \) is the dependence for \( T \);

- \( E_a \) is the apparent activation energy.
General form of the rate law for heterogeneous mineral surface reaction

\[ \text{Rate} = k_0 A \min e^{-E_a/RT} a_{H^+}^{n_{H^+}} g(I) \prod a_i^{n_i} f(\Delta G_r) \]

\( a_{H^+}^{n_{H^+}} \) is the activity of the hydronium ions in the solution; \( n \) is the order of reaction with respect to \( a_{H^+} \), i.e. pH dependance
General form of the rate low for heterogeneous mineral surface reaction

\[ \text{Rate} = k_0 A_{\text{min}} e^{-E_a/RT} a_{H^+}^{n_{H^+}} g(I) \prod_{i} a_i^{n_i} f(\Delta G_r) \]

\( g(I) \) is the possible dependance on the ionic strength of the solution

\[ I = \frac{1}{2} \sum_i c_i z_i^2 \]

\( c_i \) is the concentration of the species \( i \)

\( z_i \) is the charge of the species \( i \)

Usually negligile (between 0.01 and 0.02 M)
General form of the rate law for heterogeneous mineral surface reaction

\[ \text{Rate} = k_0 A_{\text{min}} e^{-E_a/RT} a_{H^+}^{n_{H^+}} g(I) \prod_i a_i^{n_i} f(\Delta G_r) \]

\( a_i^{n_i} \) is the activity of the species \( i \) in the solution e.g. interaction with the mineral surface. It incorporates possible catalytic or inhibitory effects on the overall rate.
General form of the rate law for heterogeneous mineral surface reaction

\[ Rate = k_0 A_{min} e^{-E_a/RT} a_H^{n_i} g(I) \prod_i a_i^{n_i} f(\Delta G_r) \]

\[ f(\Delta G_r) \] is a function of the saturation state of the solution

\[ \Delta G_r = 2.3 \log \left( \frac{IAP}{K_{eq}} \right) \]

IAP = ion activity product
\[ K_{eq} = \text{equilibrium constant} \]
\[ \log \left( \frac{IAP}{K_{eq}} \right) = \text{Saturation Index} \]
Saturation index for chrysotile and tremolite
in blood plasma, human lung and stomach tissues

From Oze C. and Solt K. (2010)

Saturation Index \((SI) = \log \left( \frac{IAP}{K_{eq}} \right)\)

**Blood Plasma**

<table>
<thead>
<tr>
<th>Elements</th>
<th>Weighted Mean* (mg/l)</th>
<th>Saturation Index†</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na</td>
<td>3162</td>
<td>Chrysotile&lt;br&gt; pH 1.2: -44.8&lt;br&gt; pH 4: -27.9&lt;br&gt; pH 7: -10.0</td>
</tr>
<tr>
<td>Cl</td>
<td>3610</td>
<td>Tremolite&lt;br&gt; pH 1.2: -103.7&lt;br&gt; pH 4: -64.3&lt;br&gt; pH 7: -22.3</td>
</tr>
<tr>
<td>Mg</td>
<td>21.2</td>
<td></td>
</tr>
<tr>
<td>Si</td>
<td>0.43</td>
<td></td>
</tr>
<tr>
<td>Ca</td>
<td>96</td>
<td></td>
</tr>
</tbody>
</table>

**Lung Tissue**

<table>
<thead>
<tr>
<th>Elements</th>
<th>Weighted Mean* (mg/l)</th>
<th>Saturation Index†</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na</td>
<td>$2220 \times 10^{-6}$</td>
<td>Chrysotile&lt;br&gt; pH 4: -44.7&lt;br&gt; pH 7: -26.3</td>
</tr>
<tr>
<td>Cl</td>
<td>$2120 \times 10^{-6}$</td>
<td>Tremolite&lt;br&gt; pH 4: -116.8&lt;br&gt; pH 7: -74.7</td>
</tr>
<tr>
<td>Mg</td>
<td>$9.84 \times 10^{-3}$</td>
<td></td>
</tr>
<tr>
<td>Si</td>
<td>$57 \times 10^{-6}$</td>
<td></td>
</tr>
<tr>
<td>Ca</td>
<td>$10.5 \times 10^{-3}$</td>
<td></td>
</tr>
</tbody>
</table>

**Gastric-Intestinal Tract Tissue (Stomach)**

<table>
<thead>
<tr>
<th>Elements</th>
<th>Weighted Mean* (mg/l)</th>
<th>Saturation Index†</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na</td>
<td>$1000 \times 10^{-6}$</td>
<td>Chrysotile&lt;br&gt; pH 1.2: -60.9&lt;br&gt; pH 7: -25.2</td>
</tr>
<tr>
<td>Cl</td>
<td>$1400 \times 10^{-6}$</td>
<td>Tremolite&lt;br&gt; pH 1.2: -154.9&lt;br&gt; pH 7: -71.5</td>
</tr>
<tr>
<td>Mg</td>
<td>$15 \times 10^{-3}$</td>
<td></td>
</tr>
<tr>
<td>Si</td>
<td>$110 \times 10^{-6}$</td>
<td></td>
</tr>
<tr>
<td>Ca</td>
<td>$11 \times 10^{-3}$</td>
<td></td>
</tr>
</tbody>
</table>

* Weighted mean values are from Iyengar et al. (1978).
† Saturation Index (SI) for each mineral was calculated using Visual MINTEQ (Gustafsson 2006) and the Lindsay database.

SI < 0 a mineral should dissolve

SI > 0 a mineral should precipitate
Fibre morphology after dissolution

Tremolite after 168 h of incubation Gamble’s solution

From Vigliaturo et al. 2018

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Surface properties and dissolution of mineral fibres.
Morphology of tremolite after dissolution

white arrows show sample breakage directions due to dissolution

From Rozalen et al. 2014
Height map of a dissolved calcite surface with etch pits measured by vertical scanning interferometry. From Luttge et al., 2005.
pH effect on the reaction kinetics

- Dissolution in batch reactor
- pH range: 1–13.5, inorganic buffered solutions, T = 25 °C
- Incubation time: 30-35 days
- Solid/solution ratio 0.5 – 2 gL⁻¹

Images of mineral fibres:
- Tremolite
- Anthophyllite
- Chrysotile
pH effect on the reaction kinetics: results of Rozalen et al. (2014)

Tremolite $\text{Ca}_2\text{Mg}_5\text{Si}_8\text{O}_{22}(\text{OH})_2$

- pH = 4

- pH = 8

Anthopyllite $\text{Mg}_7\text{Si}_8\text{O}_{22}(\text{OH})_2$

- pH = 4

- pH = 10

Chrysotile $\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$

- pH = 4

- pH = 10

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pH effect on the reaction kinetics: results of Rozalen et al. (2014)

Tremolite

Albite

Modified from Harley and Gilkes (2000)

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Surface properties and dissolution of mineral fibres.
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*Surface properties and dissolution of mineral fibres.*

**pH effect on the reaction kinetics: results of Rozalén et al. (2014)**

Tremolite

\[
\log R_{Si} = -12.13(\pm 0.02) - 0.19(\pm 0.01)pH
\]

\[
r^2 = 0.995
\]

\[
\log R_{Si} = -15.18(\pm 0.6) + 0.26(\pm 0.06)pH
\]

\[
r^2 = 0.847
\]

\[
pH = -\log[H^+]
\]

\[
a \log[H^+] = \log([H^+]^a)
\]

\[
R_{Si}(molg^{-1}s^{-1}) = 10^{-12.13(\pm 0.02)} a_{H^+}^{-0.19(\pm 0.01)} \quad pH < 6
\]

\[
R_{Si}(molg^{-1}s^{-1}) = 10^{-15.2(\pm 0.6)} a_{H^+}^{-0.26(\pm 0.06)} \quad 8 < pH < 13.5
\]
General mechanism for fibre dissolution at acidic pH

\[ R_{Si}(molg^{-1}s^{-1}) = 10^{-12.13(\pm 0.02)} a_{H^+}^{0.19(\pm 0.01)} \]
\[ R_{Si}(molg^{-1}s^{-1}) = 10^{-9.92(\pm 0.06)} a_{H^+}^{0.20(\pm 0.01)} \quad pH < 6 \text{ tremolite} \]
\[ R_{Si}(molg^{-1}s^{-1}) = 10^{-10.87(\pm 0.08)} a_{H^+}^{0.27(\pm 0.02)} \quad 1 < pH < 9.5 \text{ anthophyllite} \]
\[ R_{Si}(molg^{-1}s^{-1}) = 10^{-11.0(\pm 0.1)} a_{H^+}^{0.32(\pm 0.03)} \quad pH < 7 \text{ chrysotile} \]
Dissolution rates of different mineral fibres in inorganic solutions

modified from Rozalen et al. (2017)

\[ R_{Cr} > R_{Ant} \gg R_{Trm} \]
Effect of ligands on tremolite dissolution in mimicked lung fluids, at 37 °C in flow through reactors (Rozalén et al., 2013)

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Surface properties and dissolution of mineral fibres.
Effect of ascorbic acid on crocidolite dissolution (Martra et al., 2003)

<table>
<thead>
<tr>
<th>entry</th>
<th>suspension medium</th>
<th>amount of iron released after 25 days (μmol/g)</th>
<th>amount of monomeric silica released after 25 days (μmol/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.05 M NaCl</td>
<td>23</td>
<td>12</td>
</tr>
<tr>
<td>2</td>
<td>0.05 M NaCl + 0.01 M sodium ascorbate</td>
<td>820</td>
<td>470</td>
</tr>
</tbody>
</table>
Fibre dissolution in simulated lung fluids

Biodurability estimation using the fibre shrinking model equation (Hume, 1991)

\[ t = \frac{3d}{4V_mR} \]

- \( t \) is the residence time of the fibre (s)
- \( d \) is the fibre diameter (m)
- \( V_m \) is the molar volume (m\(^3\) mol\(^{-1}\))
- \( R \) is the dissolution rate
Fibre dissolution in simulated lung fluids

Biodurability estimation for tremolite (Rozalen et al., 2013)

- Fibre lifetime (0.1 μm diameter) is
  ~ 40 years at pH 4 and 90 years at pH 7.4.
Fibre dissolution in simulated lung fluids

Biodurability estimation for chrysotile (Hume and Rimstidt, 1992)

- Chrysotile lifetime (0.1 µm diameter) is ~ 1 month at pH 4.
- Tremolite lifetime (0.1 µm diameter) is ~ 40 years at pH 4.
- Amorphous silica lifetime (0.1 µm diameter) is ~ 100 years at pH 4.
Alteration mechanism of mineral fibres

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Surface properties and dissolution of mineral fibres.

from Gualtieri et al. (2017)
Surface alteration mechanism of amphibole asbestos: results of Pacella et al., 2014; Pacella et al., 2015

UICC crocidolite

Fibrous tremolite

- Dissolution in batch reactor
- Solution buffered at pH 7.4, with H\textsubscript{2}O\textsubscript{2} (0.1 M), T = 37 °C
- Incubation time up to 1 month
- Multi-analytical approach: ICP-OES, XPS, and TEM

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Surface properties and dissolution of mineral fibres.
Surface alteration mechanism of amphibole asbestos

**UICC crocidolite**

- Modification of fibre rim after few hours
- Severe alteration of fibre surface (with partial amorphisation)
- Formation of Fe-bearing nanoparticles after 24 h

**Fibrous tremolite**

- Absence of incipient modification
- Partial alteration of fibre surface
- Amorphous nanoparticles are only observed after 1 month

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Surface properties and dissolution of mineral fibres.
1) Incongruent dissolution takes place in the first stages of surface alteration

2) Formation of a cation depleted amorphous surface layer

3) Congruent dissolution takes place in the later stages of surface alteration

4) Fe-oxidation and formation of Fe-bearing nanoparticles during dissolution

1), 2), 3) and 4) are expected to rule the asbestos reactivity and toxicity

From Pacella et al. (2015)
Fibre batch dissolution kinetics at pH 7.4 up to 1 month

Fenton reaction

Fe\(^{2+}\) + H\(_2\)O\(_2\) → Fe\(^{3+}\) + OH\(^-\) + HO\(^-\)

Surface alteration vs chemical reactivity: results of Andreozzi et al. (2017) and Pacella et al (2018)
Surface alteration vs chemical reactivity: results of Andreozzi et al. (2017) and Pacella et al (2018)

Fenton reaction
\[ \text{Fe}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{3+} + \text{OH}^- + \text{HO} \]

The alteration process related to Maryland tremolite is the “slow-motion” of that observed for Castelluccio sample

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Surface properties and dissolution of mineral fibres.
Thanks for your attention