Fault gouge diagenesis at shallow burial depth: Solution–precipitation reactions in well-sorted and poorly sorted powders of crushed sandstone

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Abstract

Using a new oedometric-type uniaxial cell, we determine rate constants for closed-system diagenesis of crushed quartz-rich aeolian sandstone powders in distilled water, heated for weeks at \( T \sim 120° \), at pore and confining pressures of \( \sim 7 \) and 21 MPa. Results are presented for well-sorted distributions of fine and coarse size fractions, and for a poorly sorted mixture more representative of a fault gouge. The two well-sorted samples compact at nearly the same rate, but the poorly sorted gouge compacts much more rapidly at slow loading. The fine-size fraction reacts more quickly and fluids have a higher steady-state solute concentration than the coarse one. These results, combined with simple first order reaction rate theory, predict net dissolution followed by net precipitation for a simple two-phase mixture of particle sizes that is confirmed independently by the poorly sorted synthetic gouge. Observed super-saturation at relatively low effective pressures is consistent with Ostwald ripening. After the test the poorly sorted material is cemented sufficiently to be brought out as an intact, if friable, ‘rock’, indicating that fault sealing may be relatively rapid even under relatively closed conditions at depths of a few km.

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1. Introduction

The natural process that turns a loose assemblage of mineral grains such as a sediment or fault gouge into a cemented ‘rock’ in the top few kilometers of the Earth’s crust is called diagenesis. Sometimes cementation is caused by precipitation from super-saturated exotic fluids moving in from an environment with a different host rock and/or a different fluid temperature and pressure [1]. In other cases the diagenetic fluid-particle system appears closed, with localised dissolution and re-precipitation in an aqueous environment [2,3]. This requires at least temporary local thermodynamic disequilibrium and high local gradients in chemical potential, rather than the regional differences of a more open system.

In a poorly sorted mixture of grain sizes, the preferential dissolution of more chemically active smaller particles can lead to local super-saturation with...
respect to larger ones, resulting in the systematic removal of fine particles from the mixture by dissolution, and the growth of larger ones by precipitation. This process is known as ‘Ostwald ripening’ [4]. For an ideal well-sorted granular medium at high effective pressure, pressure solution is more likely to be dominant, but in more poorly sorted ones at low effective pressures Ostwald ripening can also come into play. In general, the result will be a mixture of the two processes, depending on their relative activation energies at the appropriate degree of sorting and effective pressure.

Here we examine the process resulting from local chemical disequilibrium at low effective stresses for well-sorted and poorly sorted size fractions of crushed sandstone, using a well-studied aeolian sandstone from the Clashach quarry in NE Scotland. The main aim was to establish the mechanisms and rates of diagenesis in a material that could serve as an analogue for a recently formed fault gouge at shallow depth in the Earth’s crust. The sample mineralogy and properties, and the chemical analysis techniques used to determine the pore fluid chemistry, have previously been described [5,6]. Our results were obtained at slightly lower temperatures (120 °C) than previous laboratory studies [3] of experimental diagenesis on similar plugs of unconsolidated granular pure quartz (125–225 °C), and a Labradorite sand (175 °C). We also perform the tests at lower confining pressure \( P = 20.7 \) MPa and pore pressure \( p = 6.9 \) MPa than [3], who used \( P = 100 \) MPa, \( p = 50 \) MPa. The relatively low effective pressure was chosen specifically to allow study of Ostwald ripening in fresh synthetic gouge with a range of particle sizes, in order to examine how dissolution and re-precipitation changes in a closed system with varying particle size.

2. Method

A novel experimental apparatus was designed and built to allow the study of the chemical reactivity of analogue fault gouge under isotropic confining pressure and variable pore pressure to temperatures of 120 °C [7]. A critical requirement was microlitre sampling of pore fluids during experiments, without perturbation of pore fluid pressure or chemistry. The apparatus consisted of a cylindrical stainless steel (SS) pressure cell containing opposed SS pistons driven together by a hydraulic ram in a conventional straining frame (Fig. 1a). Viton ‘O’-rings provided a fluid-tight seal between pistons and cell bore. Because fluid sampling was required from the centre of the experimental charge, the usual ‘pancake’ geometry used in oedometer-type cells, which mini-

![Fig. 1. (a) Schematic diagram of the test apparatus (upper diagram). A) cell body; B) piston; C) sample and frits; D) band heater; E) spring; F) dial gauge; G) funnel packer; H) stainless steel base packer. (b) Blow up of the sample and frit arrangement (lower diagram). A) piston; B) cell body; C) bore in piston for fluid access; D) groove in piston for sealing O-ring; E) 30 μm mesh stainless steel frit and Teflon collar; F) sample tube, G) sample pellet and Teflon tape wrap.](image-url)
central fluid sampling line. This line was a section of 0.0625 in. OD SS tube, with a SS filter embedded in its tip, exiting through the cell side wall via a swaged fitting (Fig. 1b). A 30 μm SS frit disc with Teflon edge was inserted above and below the completed powder charge, and the pistons carefully inserted. The central fluid ports axially machined into each piston were then connected to the fluid pressurisation system, the band heaters installed around the cell, and the charge allowed to thaw.

For each experiment end load and fluid pressure were raised slowly and simultaneously to their final values over a period of about 1 h. Compaction of the sample was monitored using external gauge bars with LVDTs. The full weight of the pressure vessel was supported by a pair of springs attached to the straining frame (Fig. 1a). This allowed symmetric compression of the powder charge about the centre of the cell, and prevented shearing of the side-entry fluid sampling line during loading. Fluid pressure was buffered during each run by a gas bladder accumulator system. Once the cell had been pressurised it was left for 24 h to allow the system to equilibrate, and then heated by band heaters over a period of less than 30 min to the required experimental temperature using the thermostatically controlled band heater around the cell. Run conditions for the experiments reported here were: confining pressure $P = \sigma_1 = \sigma_2 = \sigma_3 = 20.7$ MPa, pore fluid pressures $p = 6.9$ MPa, temperature 120 °C.

During heating, samples of pore fluid were regularly taken, and analysed using a Waters™ High Performance Liquid Chromatograph (HPLC) unit plumbed into the side fluid extraction port, allowing on-line analysis of the evolving pore fluid chemistry using only small volumes (microlitres) of pore fluids per analysis. This created minimal disruption to pore fluid pressures and prevented any dilution of pore fluid chemistries. On reaching the desired temperature, a further pore fluid sample was analysed and time set to zero. Following this, samples

![Particle size distribution](https://example.com/particle_size_distribution.png)

Fig. 2. Particle size distributions by (a) frequency (upper diagram) and (b) volume (lower diagram). The Diamond symbols denote the data for the bulk crushed powder, and the vertical lines define the ‘fine’ and ‘coarse’ fractions.
were taken at 12 and then 24 h, then every day for the first four days, and approximately every other day thereafter, until pore fluid chemistries reached steady state. This allowed the study of concentration change over time during creep compaction and diagenesis at constant temperature. The typical duration of the constant temperature phase (on the order of several hundred hours) is much larger than the phase of pressurisation and heating prior to the nominal ‘zero’ time (~ 26 h).

Here we report results for bulk (unsieved) crushed powder; 425–300 (coarse) and 125–75 μm (fine) size fractions of Clashach Sandstone. The particle size distributions are shown as log–log plots of frequency, Fig. 2a, and more informatively [8] of volume, Fig. 2b. To first order the bulk fraction produces a straight line on a log–log plot of frequency as a function of grain diameter. The straight line portion of the curve in Fig. 2b (between 1 and 100 μm) has a negative slope of ~2.6, similar to that of natural gouges and the self-similar fragmentation model of [9].

3. Theory

We use the generic first-order reaction rate theory applied to consecutive chemical reactions [10]. The thermodynamic and kinetic rate constants for the dissolution of silica are discussed in more detail in [11] and [12]. For the case of a single-sized fraction of quartz-rich granular material at a given $T$, $P$ and $p$, the rate of net silica dissolution, assuming a first-order reaction, is given by

$$\frac{dA}{dt} = -k_A A,$$

where $A$ is the amount of solid silica at time $t$, and $k_A$ is the reaction rate for dissolution in an aqueous environment. With the initial boundary condition $A(t=0)=A_0$, and the steady-state value $A(t=\infty)=A_{ss}$, the solution is an exponential decay

$$A = A_{ss} + (A_0-A_{ss})\exp(-k_A t),$$

However, here we measure not the weight of silica, but the quantity $I=A_0-A$ dissolved in the pore fluid:

$$I = I_{ss}[1-\exp(-k_A t)],$$

where the steady state value of $I$ is $I_{ss}=A_0-A_{ss}$. Individual smaller particles are more reactive, due to (a) their tighter radius and hence higher specific surface energy and (b) their higher specific surface area. Thus we would expect a faster dissolution rate $k_A$ for relatively fine particles. If they also have a higher steady-state concentration $I_{ss}$ in a binary mixture of ‘small’ and ‘large’ particles, then initially we would expect behaviour similar to Eq. (3), while the solution is undersaturated with respect to the large fraction (i.e. $I<I_{ss}$).

When $I>I_{ss}$, say after time $t=t_P$, Eq. (1) could no longer hold, since now material is being lost from solution due to net precipitation on the larger particles. This sequence of consecutive solution and precipitation from small to large particles is the essence of Ostwald ripening. In this case [10] we introduce a second reaction with a rate $k_b$ that produces a ‘product’ $P$ in the form of overgrowths on the larger particles. For $t>t_P$ we have to solve a coupled sequence of equations involving Eq. (1) for the reactant $A$ (small particles), along with the following two equations for the intermediate phase $I$ (dissolved silica) and the product $P$ (overgrowths):

$$\frac{dI}{dt} = k_a A - k_b I$$

and

$$\frac{dP}{dt} = -k_b I$$

subject to the boundary conditions $I(t_P)=I_{ss}^{large}=I_{ss}$, with $I$ being both continuous and differentiable at the crossover time $t=t_P$. The solution for $t>t_P$ is the same as Eq. (3) since the fluid concentration remains undersaturated with respect to $I_{ss}^{large}$. In the supersaturated case, $t \geq t_P$, we have

$$I = I_{ss}^{large} + \left(\frac{k_a}{k_b-k_a}\right) \left[ \exp\left(\frac{-k_b t}{C_{small}}\right) - \left(1 + \frac{I_{ss}^{large}}{I_{ss}^{small}}\right) \exp\left(\frac{-k_a t}{C_{small}}\right) \right] I_{ss}^{small}$$

where $I_{ss}^{small}=A_{ss}^{small}-A_{ss}^{small}$ is the steady-state concentration of the smaller particles. As $I_{ss}^{large} \to 0$ we find

$$I = \left(\frac{k_a}{k_b-k_a}\right) \left[ \exp\left(-\frac{k_b t}{C_{small}}\right) - \exp\left(-\frac{k_a t}{C_{small}}\right) \right] I_{ss}^{small}$$

This is identical in form to Eq. 25.34 of [10], for a general consecutive reaction running to zero concentration of the original reactant.

4. Results

The results for silica concentration in the pore fluid as a function of time, for fine, coarse and bulk fractions, are shown in Fig. 3a–c, respectively. The typical time for an experiment to show the full trend is on the order of several hundred hours, which is quite difficult to maintain systematically in a lab environment, so some
tests have a longer duration than others. The characteristic time for the initial dissolution reactions range from a few tens to a few hundred hours, similar to those seen in other studies of quartz dissolution (e.g. [3]; taking into account differences in temperature). The steady-state SiO$_2$ concentration ranges from $\sim 80$ ppm ($1.33 \times 10^{-3}$ mol l$^{-1}$) for the coarse fraction to $\sim 270$ ppm ($4.5 \times 10^{-3}$ mol l$^{-1}$) for the fine fraction, with the fine fraction having a much larger steady-state concentration as expected. Allowing for the surface area inferred for a given particle size distribution (determined by BET gas adsorption), the best estimate for steady-state concentration was: $2.92 \times 10^{-3}$ (fine); $8.85 \times 10^{-4}$ (coarse); and $1.18 \times 10^{-3}$ mol l$^{-1}$ (bulk). The bulk fraction shows a clear peak at 170 ppm ($2.83 \times 10^{-3}$ mol l$^{-1}$) after $\sim 200$ h, followed by a decline to $\sim 120$ ppm ($2.00 \times 10^{-3}$ mol l$^{-1}$) at 800 h (Fig. 3c), indicating super-saturation after $\sim 40$ h. No clear peak is seen in the well-sorted cases within the data scatter. All of our measured steady-state concentrations are similar within a factor two to those predicted by the solubility curve of [13], based on crushed pure quartz crystals in the size range 50–400 μm, which predicts an SiO$_2$ concentration of $1.44 \times 10^{-3}$ mol l$^{-1}$ at 120°, ignoring a small pressure correction.

Typical error bars are on the order of ±10 ppm or $\sim \pm 10\%$. The overall scatter is of a similar order of magnitude, but larger than those commonly reported in other measurements of dissolution under flow-through conditions (e.g. [12], their Fig 2.; [5], their Fig. 2). Our data scatter is more similar to that of [3] (their Fig. 13), except that at their higher temperatures there is better sampling of the steady state values within the time scale of an experimental run.

The results compare well with the solid curves formed by forward modelling of Eq. (3) for the well-sorted fractions (Fig. 3a, b) and a combination of Eqs. (3) and (6) for the poorly sorted bulk sample (Fig. 3c). A precise fit is not possible with an ideal binary model of particle sizes, but allowing for the broadening that would be expected for the finite bandwidth of sizes actually present, the model fits remarkably well, enabling reaction constants to be estimated to first order. The poorly sorted bulk material has the fastest initial dissolution rate, since it includes the finest particle sizes in absolute terms (Fig. 2), and possibly also due to the higher gradient in chemical potential in a mixed complex. The silica concentration in the pore fluid then peaks, and the last 6 points in Fig. 3c show a systematic decreasing trend, confirming that fluid super-saturation has occurred in this closed system. The asymmetry of the peak implies that the net precipitation rate after the peak is much slower than the net dissolution rate before it.

The results of the curve-fitting exercise are shown in Table 1, normalised to the measured specific surface area for each grain size distribution. The rates of the initial net dissolution reactions vary by only a factor of two, from $3.0 < k_a < 7.15 \times 10^{-10}$ mol cm$^{-2}$ s$^{-1}$, and are much less sensitive to the particle size than the
steady-state concentrations. Nevertheless the bulk sample is the most reactive in terms of initial dissolution, with the highest value for $k_a$. It also shows a decrease in concentration consistent with the precipitation of silica at a much slower rate than that of the initial dissolution ($\sim 0.25\%$ of the former). This is consistent with super-saturation of the pore fluid for this case of a poorly sorted aggregate. This demonstrates that super-saturation need not require the introduction of an exotic pore fluid in a system with a broad bandwidth of particle sizes. The net precipitation rate constant $k_b$ is much smaller than that for dissolution. Note the normalisation to specific surface area is for the initial particle size distribution, which may change to some extent during the experimental run, so the values for $k_b$, $I_{ss}^\infty$ and $I_{ss}^{\text{small}}$ are likely to be lower bounds.

The reaction constants $k_a$ and $k_b$, and the steady-state concentrations $I_{ss}^\infty$ and $I_{ss}^{\text{small}}$ are defined in the Theory section (solid lines).

The compaction curves shown in Fig. 4 reveal a much greater response for the poorly sorted bulk powder. Zero time on this curve corresponds to the end of the phase of pre-loading to the given hydrostatic effective confining pressure, equilibration and heating to the desired temperature. The $y$-axis plots the vertical (1D) compaction, in this case proportional to the volume loss in the oedometer-type cell. In contrast the two-well-sorted cases are much more resistant to creep compac-

<table>
<thead>
<tr>
<th>Size fraction</th>
<th>$k_a$ (mol cm$^{-2}$ s$^{-1}$)</th>
<th>$k_b$ (mol cm$^{-2}$ s$^{-1}$)</th>
<th>$I_{ss}^\infty$ (mol l$^{-1}$)</th>
<th>$I_{ss}^{\text{small}}$ (mol l$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a) Fine</td>
<td>$3.0 \times 10^{-10}$</td>
<td>$-2.0 \times 10^{-4}$</td>
<td>$2.0 \times 10^{-12}$</td>
<td>$-2.5 \times 10^{-3}$</td>
</tr>
<tr>
<td>(b) Coarse</td>
<td>$5.0 \times 10^{-10}$</td>
<td>$-8.85 \times 10^{-4}$</td>
<td>$8.5 \times 10^{-12}$</td>
<td>$-2.5 \times 10^{-3}$</td>
</tr>
<tr>
<td>(c) Bulk</td>
<td>$7.15 \times 10^{-10}$</td>
<td>$1.15 \times 10^{-12}$</td>
<td>$1.18 \times 10^{-3}$</td>
<td>$2.35 \times 10^{-3}$</td>
</tr>
</tbody>
</table>

Fig. 4. Compaction curves (measured on the pistons at locations shown in Fig. 1b) for the fine, coarse, and bulk samples.

Fig. 5. Photomicrographs of thin section of the sample taken after the test for: the bulk gouge material (upper diagram); the coarse fraction (middle diagram) and the fine fraction (lower diagram).
Fig. 5. This also highlights the differences in the materials in terms of sorting. Due to the very small amount of dissolved or precipitated material, no obvious induration is seen, and it is not possible uniquely to identify overgrowths as belonging to the Ostwald ripening process over the time scales seen here. This highlights the utility of HPLC when very small volumetric changes, visually undetectable in the solid sample, are involved at low temperature/pressure.

5. Discussion

The results presented here form a first experimental glimpse into the conditions in which Ostwald ripening may act as a mechanism for diagcnosis in a fault gouge at geologically low temperatures and effective pressures. By dissolving small particles and precipitating overgrowths on larger ones, the material will become stronger due to this effective cementation. This is consistent with the experimentally observed time-dependent increase in fault gouge strength reported by [14] and [15]. In [15] the results are interpreted as being due primarily to pressure solution. However, by removing the fine particles systematically, and maintaining the same arrangement of larger ones, Ostwald ripening may accelerate the cementation process. In the absence of ongoing shear, the resulting better-sorted particle size distribution may then have a more ordered pore structure, with the same porosity but perhaps a higher permeability. Under conditions of higher effective stress, higher temperature, finite shear stress or strain [3] a more disordered structure occurs due to grain crushing, pressure solution, and particle rearrangement that appears instead systematically to decrease the porosity and permeability with time. The results presented here illustrate only one part of the spectrum of phenomena in the rich diversity of behaviour that may be anticipated in fault gouge due to a plethora of competing effects.

A second point of discussion is the applicability of a binary particle size model to the results. Clearly the bulk crushed powder (and even the sieved size fractions) actually have a finite bandwidth of sizes (Fig. 2). It is quite possible, perhaps having to resort to numerical methods, to extend the theory developed above to a spectrum of sizes, but it is not clear at this stage if the additional parameters would be justified within the data scatter. One qualitative result that can be anticipated with confidence for the synthetic fault gouge, is a broader peak, more consistent with the data in Fig. 3c.

A major caveat in applying these results to the Earth is the effect of differences in the pore fluid chemistry. In a closed system in the Earth the pore fluid is likely to be in much closer chemical equilibrium than the far-from equilibrium conditions we have examined here. For example connate pore waters are likely to be in much closer chemical equilibrium with any gouge material produced in a later faulting episode. They also contain salts in solution that are known to strongly affect the dissolution rates of quartz, even in small concentrations [12]. As a consequence, the results here should not be applied directly to the interpretation of field data without taking these systematic differences into account. Rather they provide a simple model that may be applied with some changes in the effective model parameters. These systematic differences are most likely to take the form of much slower reaction rates, with steady-state concentrations perhaps being affected to a lesser degree. For example a recent paper inferring rates of fault healing in the crust at earthquake nucleation depths indicates healing times on the order of two years [16].

Finally, our results – ultimately constrained by the low stability field of temperatures of the test apparatus, the random element of the stability of long-term experimental rock physics/chemistry tests, and the low fluid sampling volumes – do not always sample the long-term steady state values very well. Practical advances in online HPLC analysis techniques are required to address this problem.

6. Conclusion

We have experimentally reproduced the conditions for Ostwald ripening in a closed system of distilled water and poorly sorted bulk crushed powder from a quartz-rich aeolian sandstone. Simple first-order kinetics for the consecutive reactions of dissolution of fine particles and precipitation on larger ones produces an adequate fit to the data. The reaction rates are geologically extremely fast, with characteristic transient times on the order of a few days or weeks, but compare reasonably with other studies, allowing for the differences in temperature and initial chemical disequilibrium. The long-term steady state values have finite irreducible uncertainties, but finer particles have higher steady-state concentrations than coarser ones within these error bounds. A clear peak and a post-peak reduction in silica concentration is observed, consistent with the local super-saturation and high chemical potential gradients inherent in the Ostwald ripening process.

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