Chapter 3

COMPACTION CREEP OF QUARTZ-MUSCOVITE MIXTURES AT 500 °C: PRELIMINARY RESULTS ON THE INFLUENCE OF MUSCOVITE ON PRESSURE SOLUTION


Abstract

It is widely claimed that the presence of phyllosilicates in sandstones increases intergranular pressure solution (IPS) rates in these rocks. However, this has not been experimentally confirmed. This study reports the results of isostatic hot-pressing compaction experiments at a temperature of 500 °C and an effective pressure of 100 MPa on mixtures of quartz and muscovite. Previous work has shown that under these conditions dissolution is rate controlling in pure quartz. No acceleration of compaction of quartz by the addition of muscovite was observed. Instead, a modest decrease in IPS rates was observed (factor 3-10), which we infer was due to a decrease in IPS rate. The effect of muscovite in slowing IPS may be due to the influence of dissolved aluminium (Al\(^{3+}\)) dominating over any accelerating effects of alkali-metal cations. From the geochemical literature, Al\(^{3+}\) in solution is expected to decrease the solubility, dissolution rates and precipitation rates of quartz. However, the effect of the addition of muscovite on IPS rates in quartz when controlled by diffusion or precipitation may be different. Experiments should be conducted on quartz sand under conditions where diffusion or precipitation is rate controlling to investigate these effects.

3.1. Introduction

From microstructural evidence, it is widely accepted that intergranular pressure solution (IPS) is an important compaction, lithification and deformation mechanism in clastic sediments under diagenetic and low-grade metamorphic conditions (Rutter, 1983; Tada and Siever, 1989). IPS exerts a strong influence on porosity and permeability reduction in sandstones and mudstones, and hence on reservoir and top-seal evolution in sedimentary basins (Addis and Jones, 1985; Houseknecht, 1987; Rutter and Wanten, 2000). It is also likely to play an important role in controlling strength recovery and seismic vs. frictional-viscous slip on gouge-bearing crustal faults ((Bos et al., 2000a, b; Bos and Spiers, 2000, 2001).

Despite the importance of IPS in siliciclastic sediments and quartz-phyllosilicate fault gouges, the rate controlling mechanism and kinetics of IPS in quartz are still poorly constrained, principally because of the slowness of the process under lab conditions. Recent experimental work has suggested that when there is no long range advective or diffusive transport, IPS in pure quartz sand is probably controlled by the kinetics of quartz dissolution, at least at porosities down to ~15% (see Chapter 2). Regarding the effects of
phyllosilicates, numerous field and petrographic associations between phyllosilicate content and enhanced IPS or pressure solution seams (e.g., Heald, 1959; Rutter, 1983; Engelder and Marshak, 1985; Tada and Siever, 1989; Renard et al., 1997) have led to the view that phyllosilicates dramatically increase IPS rates in quartz, presumably via enhanced grain boundary diffusion or enhanced reaction kinetics. However, the influence of phyllosilicates on IPS rates in quartz has remained largely unexplored from the experimental and theoretical points of view.

Though few experiments have been done on the influence of phyllosilicates on IPS, two recent studies indicate strong enhancement effects. Hickman & Evans (1995) studied pressure solution rates at halite-silica contacts by pressing a convex halite lens against a fused silica plate under brine. One experiment was conducted in which the silica plate was coated with a 0.8-μm-thick film of Na-montmorillonite. The presence of the clay film produced an approximately fivefold increase in pressure solution convergence rate over clay-free experiments conducted under otherwise identical conditions. Assuming diffusion to be rate-limiting, as observed in their halite-silica experiments, Hickman & Evans (1995) calculated an effective grain boundary (clay layer) diffusivity about 30 times greater than for the halite-silica interfaces. Montmorillonite was used as the phyllosilicate phase because of its propensity for extreme swelling through incorporation of interlayer water. The observed increase in effective grain boundary diffusivity per unit clay layer thickness is therefore likely to represent the maximum effect of phyllosilicates on pressure solution rate enhancement, when diffusion is rate controlling. However, in other materials such as quartz, where interface reactions may be rate controlling, where different surface forces may come into play at contacts with phyllosilicates, and where surface reactions may be influenced by chemical effects of phyllosilicates present, the influence of phyllosilicates on IPS may be quite different.

In the second recent study, Rutter & Wanten (2000) investigated IPS rates by hot isostatic pressing of samples consisting of granular quartz embedded in a matrix of fine-grained illite and muscovite, with a small adjacent volume of porous quartz sand to provide a sink for precipitation of silica dissolved from the phyllosilicate-quartz mixture. The presence of phyllosilicates in the matrix strongly enhanced compaction rates compared to pure quartz samples. Rutter & Wanten argue that this was caused by enhancement of pressure solution of the quartz at quartz/phyllosilicate contacts and by a strain contribution due to intracrystalline plasticity plus frictional flow in the phyllosilicates. However, they give no suggestions about the rate-limiting process controlling IPS. Their experiments are indeed difficult to interpret since, compared with the pure quartz sand samples, the introduction of the phyllosilicate matrix leads to changes in the stresses transmitted across quartz grain surfaces (hence in the driving force for IPS), in the source-sink diffusion path, in the areas available for quartz dissolution and precipitation, in the chemistry and pH of the pore fluid and probably in the state of the intergranular fluid. As all of these factors can potentially influence the rate and/or rate controlling mechanism of IPS, the exact effect of
the phyllosilicates on IPS in quartz is hard to deduce from the experiments of Rutter & Wanten (2000).

It is thus evident that while there are ample indications in nature for an influence of phyllosilicates on IPS rates in quartz rich rocks, the effect has yet to be confirmed, mechanistically identified, or systematically characterized in laboratory experiments. This preliminary study consists of compaction experiments on quartz-muscovite mixtures at a confining pressure of 300 MPa, a pore fluid pressure of 200 MPa and a temperature of 500 °C, and extends our previous study of IPS in pure quartz sand under similar conditions (Chapter 2). In that study, we found that IPS dominated over both cataclasis and dislocation creep, and we concluded that IPS rates were controlled by the quartz dissolution reaction at grain contacts. Here, we attempt to systematically examine the effect of adding sufficient muscovite to coat grain contacts, without filling all the intergranular pore space.

3.2. Background Considerations

In a chemically closed system (no removal or addition of solid mass by long range diffusive or advective transport in the pore fluid), compaction of a fluid-saturated granular aggregate, by intergranular pressure solution (IPS), involves dissolution of solid material at stressed grain-to-grain contacts, diffusion of this material through the intergranular fluid into the open pores, followed by precipitation on the free pore walls. The process is driven by differences in effective normal stress, hence the normal component of the solid chemical potential, between grain contacts and free pore walls (e.g.. Lehner, 1990). Under steady state conditions, any of the three mechanisms of dissolution, diffusion and precipitation may be rate controlling (De Meer and Spiers, 1995). When we wish, as in the present study, to investigate the influence of phyllosilicates on IPS rates in quartz, it is therefore useful to first consider what, in theory, their influence on the three serial processes of IPS can be. These considerations form the basis for our choice of experimental method.

We begin by briefly considering the physical and chemical properties of phyllosilicates, especially the surface properties in the presence of water. Phyllosilicates are characterised by \([\text{SiO}_4]\) tetrahedra linked together to form flat sheets with the composition \([\text{Si}_4\text{O}_{10}]\). This group of minerals includes muscovite, biotite, phlogopite, chlorite, clays, talc and serpentine, all of which are soft, plastically deformable minerals of variable but generally low density, and which always contain a specific amount of structurally bound water.

Muscovite, the mineral used in this study, belongs to the mica sub-group and is characterised by a 2:1 layering, i.e. a periodic structure consisting of 2 tetrahedral sheets \([\text{Si}_4\text{O}_{10}]\), and one octahedral \([\text{Al}_2(\text{OH})_6]\) sheet repeated throughout the mineral structure (Deer et al., 1977). Muscovite (and mica in general) always contains a variable amount of structurally bound water, in the form of hydroxyl ions in the octahedral sheets (Deer et al., 1977). Cation substitution in the tetrahedral sheets (i.e. \text{Al}^{3+} for \text{Si}^{4+}) results in an overall negative charge on the tetrahedral layers. The charge is compensated, and the layers bonded
together by large, positively charged interlayer cations, most commonly $K^+$, $Na^+$ or $Ca^{2+}$. However, as a result of substitution of $Si^{4+}$ by $Al^{3+}$ in the tetrahedral sheets, freshly cleaved muscovite (and mica in general) has a negative surface charge under vacuum. In aqueous solution protons will sorb to the surface of the muscovite to balance the negative charge. The pH at the point of zero charge ($pH_{pzc}$, i.e. the pH of the solution at which the surface is electrically neutral) of muscovite in an aqueous solution has been calculated to be 6.6 (Sverjensky, 1994).

When diffusion is the rate controlling process of IPS, the effect of phyllosilicates on IPS rates in quartz is expected to be one of accelerating pressure solution (Hickman & Evans 1995; Renard et al. 1997; Rutter & Wanten 2000). This expectation is mainly based on measurements of the disjoining pressure acting between quartz-quartz and quartz-mica surfaces (Figure 3.1). For a flat, interfacial fluid film, the disjoining pressure equals the amount by which the fluid pressure acting on the fluid-solid interface exceeds the hydrostatic pressure in the bulk fluid. In general, it is believed to be caused mainly by hydration forces (i.e. forces which result from the short range ordering of water molecules along the solid/liquid interface) and not by van de Waals interactions or electrical double-layer repulsion, since these can not explain the observed forces (Heidug, 1995; Hickman and Evans, 1995). In the case of stressed granular solids, the disjoining pressure in an interfacial fluid film balances the effective compressive stress to maintain an open, wetted grain boundary with a stress-dependent thickness. The various measurements imply that quartz/mica interfaces can support a thicker layer of water in the grain boundary than quartz/quartz interfaces at a given normal stress. At a film thickness of 1 nm a mica/mica interface can support ~10 times more stress than a quartz/quartz interface, see Figure 3.1. (Pashley and Israelachvili, 1984; Heidug, 1995; Renard et al., 1997). At a quartz/quartz interface van der Waals forces are attractive and the surface charge is low, resulting in only weak ordering of water molecules and thus in weak hydration forces. At a quartz/mica interface however, van der Waals forces are repulsive and the surface charge (of the mica) is high, resulting in strong ordering of water molecules and thus in strong hydration forces, ultimately leading to a higher fluid film thickness than at a quartz/quartz interface at similar stresses. Nonetheless, at sufficiently high intergranular stresses, water will be squeezed out, even from a quartz-mica interface (Israelachvili, 1992; Heidug, 1995). When dissolution or precipitation is the rate controlling process, the influence of muscovite on pressure solution rate can be chemical.
or physical. First, the presence of muscovite in quartzitic rocks changes the chemistry of the pore fluid by (in)congruent dissolution of the muscovite (typical dissolution rate at 70 °C and a pH of 6.2 is \( \sim 10^{-16} \text{ mol/cm}^2\text{s} \); (Knauss and Wolery, 1989). This releases cations (e.g., \( K^+ \), \( Al^{3+} \)) into the solution, and/or modifies the pH of the pore fluid. When the pore fluid contains alkali-metal or alkali-earth ions, or has a non-neutral pH, the solubility and interfacial reaction rates of quartz are increased by approximately one order of magnitude, depending on the concentrations of the cations (Dove and Rimstidt, 1994; Dove and Nix, 1997; Renard et al., 1997; Dove, 1999). This will increase the IPS dissolution rate, the diffusive transport rate and the precipitation rate, so that IPS rates will increase. However, the presence of a minute amount of aluminium in the pore fluid (as low as 0.15 ppm equivalent of \( Al_2O_3 \)) can strongly decrease the apparent solubility of quartz as well as dissolution and precipitation rates (Iler, 1973, 1979; Mullis, 1993; Dove and Rimstidt, 1994) presumably by adsorption of \( Al^{3+} \) onto quartz surfaces. The amount of decrease in dissolution/precipitation rates, however, remains unclear. Estimates vary from 3 to as much as 8 orders of magnitude, but the effect may be much smaller (~1 order of magnitude, Dove, pers. comm.). Moreover, the presence of muscovite in pore spaces, and on pore walls, decreases the area available for precipitation on the quartz surface (Tada and Siever, 1989; Dewers and Ortoleva, 1991; Mullis, 1993), resulting in a decrease in overall precipitation rate. Thus, the presence of phyllosilicates in general, and muscovite in particular, can increase or decrease IPS rates in quartz. In addition, the reaction mechanism at a quartz-muscovite interface may be completely different from that at a quartz-quartz interface, due to a different surface charge, a different pH and the presence of cations such as \( Al^{3+} \) and \( K^+ \).

Finally, it is important to note that the presence of phyllosilicates may cause a change in rate controlling mechanism of IPS, compared with a pure quartz rock, through any of the above-mentioned effects on dissolution, diffusion and precipitation rates.

### 3.3. Experimental method

Our experiments consisted of isostatic compaction or hot-pressing (HIPing) experiments carried out on wet quartz sand with 0-20 wt% added muscovite. The temperature used was 500 °C, the confining pressure was 300 MPa, the pore fluid pressure 200 MPa and the effective pressure thus 100 MPa. The experiments were carried out using the same starting material as used by Niemeijer et al. (2002, Chapter 2) in their study of IPS in quartz, namely quartz sand from the Miocene “Bolderiaan” formation, Belgium. The material had previously been refined in a ball-mill, ultrasonically cleaned in distilled water and etched in HF solution to remove surface damage. We sieved the product to obtain a starting grain size fraction of 45-75 μm. Muscovite additive was prepared using natural muscovite from Norway. This was crushed in a ball mill and the resulting powder sieved to obtain fractions of 45-90 and < 28 μm. This was in turn mixed with the sieved quartz sand, in different ratios, to obtain 5, 10 wt% and 20 wt% muscovite-quartz samples, in addition to several pure quartz samples.
3.3.1. Apparatus and Procedure

The apparatus used is described in Chapter 2. It consists of a cold seal "Tuttle bomb" pressurized with Argon, plus an internal sample/capsule assembly linked to an independent pore fluid system (Figure 3.2.). The pore fluid and Argon pressures were measured with a Bourdon-type pressure gauge (resolution ~ 1 MPa) and/or a pressure transducer (resolution ~ 0.2 MPa). The temperature of the sample was measured using a pre-calibrated K-type thermocouple embedded in the bomb wall (error of ~2 °C).

In each experiment, ~2 grams of quartz-muscovite mixture were loaded into the annealed copper capsule assembly via the "top cup" end (enlargement Figure 3.2.). The capsule was then sealed by pressing- and welding-in the copper "top cup" (Figure 3.2.), producing a sample porosity of ~45-50%. The sample assembly was subsequently loaded into the Tuttle bomb, evacuated and flooded with water from the pore fluid reservoir. Each sample was then Cold Isostatically Pressed (CIPed) at a confining pressure of 300 MPa for 30 minutes, with the pore pressure maintained close to 0.1 MPa (1 atm.). This was done to produce a reproducible starting porosity and microstructure for the hot pressing stage (cf. Spiers and Brzesowsky, 1993; De Meer and Spiers, 1995) and to minimize strain due to grain rearrangement and cataclasis during HIPing at 100 MPa. The confining pressure was subsequently reduced to ~140 MPa and the pore fluid pressure raised to ~135 MPa using the volumometer pump. The sample was then heated at ~15 °C per minute. During heating, the effective pressure was maintained as low as possible and was always <10 MPa. After

![Figure 3.2.: Schematic diagram of the experimental apparatus with an enlargement showing the capsule/sample set-up.](image-url)
attaining thermal equilibrium at the desired test temperature (500 °C) and confining pressure (300 MPa), the required effective pressure was applied by extracting fluid from the sample using the volumometer. The confining and pore fluid pressures were subsequently kept within ± 5 MPa of the desired values. The minimum measurable fluid volume increment was ~2 μl, yielding an absolute resolution in volumetric strain at room temperature of ~0.02 %.

Experiments were terminated when the pore volume loss was no longer detectable via changes in pore fluid pressure. At this stage, the bomb was quenched, using compressed air, at an average cooling rate of ~30 °C per minute. The indurated sample was then removed from the apparatus and capsule and dried in an oven at 60 °C for 24 hours. The final porosity (φf) of the sample was measured by wrapping it in ultra-thin plastic film and determining its volume (Vf) using the Archimedes method and density data on quartz and muscovite (Deer et al. 1977). The samples were finally impregnated with epoxy resin and sectioned for optical and SEM study.

3.3.2. Data Acquisition and Processing

As indicated above, pore volume loss during the experiments was determined incrementally by measuring the volume of fluid extracted from the sample to maintain constant pore pressure. The volume of muscovite was assumed to be constant and thus of no direct influence on porosity reduction. The measurements were accurately corrected for density changes associated with the cooling of the pore fluid during extraction, using appropriate P-V-T equations for water (Burnham et al., 1969). The "starting porosity" (φ0) of the sample, i.e. before HIPing at the test temperature, was calculated by adding the total amount of fluid expelled from the sample during HIPing to the final pore volume (φf, Vf) of the sample. The difference in the pore and sample volumes, measured at room temperature and pressure compared to the post-HIPing volumes at test conditions, can be estimated using the bulk modulus of sandstone (~2.5-7.5·10¹¹ Pa, Birch 1966) and the volumetric thermal expansion coefficient of quartz (~4-5·10⁻⁵ K⁻¹, Skinner 1966) and was found to be negligible. The overall relative standard error in volume measurements was approximately 5 %, implying an absolute standard error in the porosity measurements of less than 0.2 %. The volumetric strain rate associated with individual data was calculated using the 2 point central difference method.

3.3.3. Dry Control Runs

Control HIPing experiments on "dry" sand fractions were performed in the same apparatus as the wet tests, but using fully sealed capsules with no added water. The "dry" samples were first CIPed at 300 MPa for 30 minutes and their porosities determined at atmospheric pressure using the Archimedes method. The samples were then HIPed at 500
°C and pore volume loss was measured periodically by removing the capsule from the bomb and re-determining its total (current) volume.

3.4. Results

3.4.1. Mechanical Data

The complete set of experiments reported here is listed in Table 3.1., along with data on the starting and final porosities of the samples and the total volumetric strains achieved. The CIPed-only quartz sand sample (D9) showed compaction from ~45% porosity to ~30% (Table 3.1.). Compaction creep data obtained during HIPing of the wet quartz-muscovite samples (CPf 10, 11, 12, 13), the wet quartz only sample (CPf 3) and the "dry" sand sample (D17) are presented in Figure 3.3a. in the form of \( \phi/\phi_0 \) vs. time curves. These demonstrate time-dependent compaction in all samples. The "dry" control sample (D17) shows relatively slow compaction and modest final strain (Table 3.1.). By contrast, the wet, quartz-only sample (CPf 3) compacted very rapidly in the first ~12 hours of the experiment, halving its porosity in that time. The wet muscovite-quartz samples (CPf 10, 11, 12 and 13) compacted more slowly initially, but attained similar final porosities and porosity reduction rates after 3-4 days. Note that the curves of samples CPf 10, 11 and 12 are closely similar, although sample CPf 12 seems to maintain a higher strain rate to lower values of \( \phi/\phi_0 \). Sample CPf 13 (5wt% muscovite) compacted slightly faster than CPf 10, 11 and 12, but still more slowly than the quartz-only sample (CPf 3). Figures 3b and 3c show compaction rate data computed for the dry and wet samples (0 wt%, 5 wt%, 10 wt%, 45-75 μm and <28 μm and 20 wt% muscovite) versus normalized porosity \( \phi/\phi_0 \). Normalized porosity was used rather than volumetric strain or absolute porosity since this quantity reduces the influence of variations in starting porosity upon strain rate as discussed by Niemeijer et al (2002 and Chapter 2). Figure 3.3b shows compaction rate data computed for the dry and wet samples (0 wt%, 10 wt% and 20 wt% muscovite) versus normalized porosity \( \phi/\phi_0 \). It demonstrates that the dry sample (D17) compacted at rates 1-3 orders of magnitude slower than the wet samples at given strain \( (\phi/\phi_0) \). The fits shown in Figures 3.3b and c were used to construct plots of compaction strain rate versus muscovite content for the wet samples (CPf 3, 10, 11 and 13) at constant \( \phi/\phi_0 \) values (Figure 3.3c.). Both Figures 3.3b. and 3.3c. show a decrease in strain rate of 0.5-1 order of magnitude, caused by addition of muscovite, with no further reduction in the range 10-20 wt% muscovite.
Table 3.1: List of experiments performed showing initial (pre-HIPing) porosities ($\phi_0$), final porosities ($\phi_f$), wt\% muscovite and isostatic pressing conditions. T denotes test temperature, Pc confining pressure, Pf pore fluid pressure and Pe the applied effective pressure. "Dry" means no water added.

Starting or pre-HIPing porosity measured under atmospheric conditions, i.e. after CIPing. * Starting or pre-HIPing porosity calculated for loaded conditions from the final porosity and porosity change determined during HIPing. † Fraction of <28 μm muscovite used, ‡ Fluid pressure measured with High Pressure transducer.

<table>
<thead>
<tr>
<th>Sample number</th>
<th>T (K)</th>
<th>wt% muscovite</th>
<th>Pc (MPa)</th>
<th>Pf (MPa)</th>
<th>Pe (MPa)</th>
<th>$\phi_0$ (%)</th>
<th>$\phi_f$ (%)</th>
<th>Total volumetric strain(%)</th>
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<tr>
<td>D 9</td>
<td>298</td>
<td>0</td>
<td>300</td>
<td>-0.1</td>
<td>-300</td>
<td>30.31</td>
<td>30.31</td>
<td>-</td>
</tr>
<tr>
<td>D 17</td>
<td>773</td>
<td>0</td>
<td>60</td>
<td>&quot;dry&quot;</td>
<td>60</td>
<td>27.17†</td>
<td>19.65</td>
<td>9.06</td>
</tr>
<tr>
<td>CPI 3</td>
<td>773</td>
<td>0</td>
<td>300</td>
<td>200</td>
<td>100</td>
<td>27.31†</td>
<td>12.71</td>
<td>16.70</td>
</tr>
<tr>
<td>CPI 10++</td>
<td>773</td>
<td>10</td>
<td>300</td>
<td>200</td>
<td>100</td>
<td>24.46†</td>
<td>10.52</td>
<td>15.56</td>
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<tr>
<td>CPI 11++</td>
<td>773</td>
<td>20</td>
<td>300</td>
<td>200</td>
<td>100</td>
<td>24.53†</td>
<td>10.30</td>
<td>15.84</td>
</tr>
<tr>
<td>CPI 12+++*</td>
<td>773</td>
<td>10</td>
<td>300</td>
<td>200</td>
<td>100</td>
<td>22.17†</td>
<td>8.31</td>
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<tr>
<td>CPI 13+++</td>
<td>773</td>
<td>5</td>
<td>300</td>
<td>200</td>
<td>100</td>
<td>24.15†</td>
<td>9.51</td>
<td>16.00</td>
</tr>
</tbody>
</table>
Figure 3.3: Compaction creep data showing influence of muscovite.
(a): Compaction creep curves in the form of $\phi/\phi_0$ vs. time plots for the samples D17, CPf 3, CPf 10 and CPf 11. Inset shows compaction creep curves in the first 5 hours.
(b): Log (strain rate) vs. $\phi/\phi_0$ plots with linear best fits for samples D17, CPf 3, CPf 11, and CPf 13.
(c): Log (strain rate) vs. $\phi/\phi_0$ plots with linear best fits for samples CPf 3, CPf 10 and CPf 12.
(d): Log (strain rate) vs. wt% muscovite curves showing the influence of muscovite on compaction rates in wet samples CPf 3, CPf 10, CPf 11 and CPf 13.
3.4.2. Microstructural Observations and Compositional Data

The starting fraction of Bolderiaan Sand consisted of > 99% quartz (Chapter 2). Our optical and SEM observations showed the quartz grains to be subangular to angular with surfaces characterized by triangular, pyramidal and sickle-shaped etch pits. The sieved fraction of the natural muscovite was analysed using x-ray diffraction (XRD), inductively coupled plasma mass spectrometry (ICP-MS) and thermogravimetric analysis (TGA). The material consists of > 99% muscovite, with the chemical composition given in Table 3.2.

Optical microscopy and SEM observations made on both CIPed-only material (D9- equivalent to the "starting material" for the HIPing samples) and "dry" HIPed sample (D17) show closely similar microstructures characterized by widespread intragranular and transgranular cracks, grain size reduction and sharp grain contact points (Figure 3.4a.). We found no microstructural evidence that dissolution/precipitation processes were active in these samples. The final grain size of all wet-HIPed samples (CPF 3, 10 and 11) was reduced compared to the starting sand fractions, but much less than in the cold compacted sample (compare Figures 3.4a-d, see also Chapter 2). In all wet-HIPed samples (Figures 3.4b-d) fewer fine grain fragments and fewer cracks were observed than in the CIPed only material (Figure 3.4a), suggesting that many of the finest cataclastic fragments seen in the cold-pressed material dissolved during HIPing and that some cracks may have healed. All wet samples show tightly fitting, often micro-sutured grain boundaries and concave-convex grain-to-grain contacts (indentations and truncations), indicative of IPS (Figures 3.4b-d). We observed only a few intragranular fractures associated with well-fitting or indented grain contact, suggesting that interaction between fracturing and pressure solution (Gratier et al., 1999) did not play an important role in our experiments. Minor undulatory extinction is visible optically in the quartz grains, but the total fraction of quartz grains showing this is less than 5%. Muscovite sheets in the muscovite-bearing wet-tested samples almost always show some undulatory extinction (Figures 3.4c-d). They are often sharply "bent" around the quartz grains with no clear indication of fracturing. Muscovite sheets have not developed a preferred orientation, nor do they form a continuous network in 2-D section.

### Table 3.2:

<table>
<thead>
<tr>
<th>Composition</th>
<th>wt%</th>
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<tbody>
<tr>
<td>SiO₂</td>
<td>43.35</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>34.53</td>
</tr>
<tr>
<td>K₂O</td>
<td>10.93</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>4.40</td>
</tr>
<tr>
<td>MgO</td>
<td>1.21</td>
</tr>
<tr>
<td>Na₂O</td>
<td>0.53</td>
</tr>
<tr>
<td>CaO</td>
<td>0.10</td>
</tr>
<tr>
<td>BaO</td>
<td>0.14</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.15</td>
</tr>
<tr>
<td>H₂O</td>
<td>4.61</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>99.85</strong></td>
</tr>
</tbody>
</table>

The chemical composition of natural muscovite (fraction 45-90 μm) determined by ICP-MS analyses. Other elements are less than 0.1 wt%. H₂O-content was determined by TGA.
Figure 3.4: Microstructures characterizing the various experiments.
(a): SEM backscatter image of sample D9 (CIPed-only sample, $P_c=300$ MPa, $P_f=0.1$ MPa, $\phi_f=30.31\%$)
(b): SEM backscatter image of sample CPf 3 (wet compacted sample, $P_c=300$ MPa, $P_f=200$ MPa, 0 wt% muscovite, $\phi_f=12.71\%$), showing grain-to-grain indentations and truncations (black arrows) indicative of IPS.
(c): Reflected light micrograph of sample CPf 10 (wet compacted sample, $P_c=300$ MPa, $P_f=200$ MPa, 10 wt% muscovite, $\phi_f=10.52\%$), showing grain-to-grain indentations and truncations (black arrows) indicative of IPS.
(d): SEM backscatter image of sample CPf 12 (wet compacted sample, $P_c=300$ MPa, $P_f=200$ MPa, 10 wt% muscovite <28 $\mu$m, $\phi_f=8.31\%$), showing grain-to-grain indentations and truncations (white arrows) indicative of IPS.
3.5. Discussion

Using identical methods and identical quartz sand, Niemeijer et al. (2002 and Chapter 2) demonstrated that IPS dominates the compaction of quartz sand at 400-600 °C and effective pressures of 50-150 MPa, and is probably controlled by the quartz dissolution reaction rate. Our present microstructural results show evidence for IPS in both quartz-only and quartz-muscovite samples under the same conditions. The mechanical data demonstrate that the presence of muscovite hinders rather than enhances compaction. The amount of muscovite in the samples was too low to form a continuous network or to completely fill the pore space, suggesting that the muscovite did not form a load supporting matrix, so that the quartz grain framework must have supported almost as much of the applied effective pressure as in the pure quartz sand samples. Plastic deformation of intergranular micas could have modestly hindered compaction or enhanced it by promoting grain boundary sliding between quartz grains. However, since IPS was clearly important in all wet samples, we infer that the presence of muscovite did not enhance IPS rates dramatically, but may even have decreased IPS rates.

Recalling the possible effects of phyllosilicates on IPS rates which we have already identified, a decrease in IPS rate due to the addition of muscovite could potentially be explained by dissolution of aluminium from the muscovite in the pore fluid, the dissolved Al\(^{3+}\) then lowering the solubility of quartz and slowing the dissolution and precipitation kinetics of quartz (Iler, 1973, 1979; Dove and Rimstidt, 1994). The amount of Al\(_2\)O\(_3\) equivalent in solution after heating (~1 hour) was calculated using the only data we know of on the dissolution kinetics of muscovite (Knauss and Wolery, 1989). We extrapolated Knaus and Wolery’s dissolution rate data obtained at 70 °C to the temperature conditions of our experiments using their activation energy of 59 kJ/mol. The results obtained was of the order of ~0.8 ppm Al\(_2\)O\(_3\) equivalent for sample CPf 10, which is sufficient to lower dissolution rates of quartz by a measurable amount according to previous work on the effects of Al\(^{3+}\) (Iler, 1973, 1979).

However, muscovite can also hinder the precipitation of quartz by decreasing the number of precipitation sites on pore walls (Tada and Siever, 1989; Dewers and Ortoleva, 1991; Mullis, 1993). This could cause a shift in rate controlling mechanism from dissolution towards precipitation, decreasing IPS rate accordingly. If in a pure quartz aggregate the grain boundary fluid occupies an open island-channel structure, rather than an ultra thin film maintained by surface forces, the presence of muscovite in the quartz grain boundaries could possibly retard diffusion of quartz out of the boundaries by supporting a thin fluid film which replaces the more open island-channel structure. This would cause a shift in rate controlling mechanism from dissolution to diffusion, again decreasing IPS rates. It is even possible that in our experiments contact stresses may have been high enough to squeeze water out of some mica-quartz contacts (Israelachvili 1992).

Our microstructural observations do not exclude any of the above explanations for a possible reduction in IPS rates due to the addition of muscovite, since it was present in
quartz grain contacts actively undergoing IPS and at the pore walls. However, our mechanical data show that the decrease in compaction rates caused by adding muscovite does not seem to depend strongly on the amount of muscovite added (5 wt% vs. 10 wt% and 20 wt%). This suggests that the observed decrease in IPS rate was caused by a chemical effect, such as a decrease in dissolution rate due to saturation of the pore fluid with $\text{Al}^{3+}$, rather than an effect of muscovite coating grain boundaries or pore walls, or filling the pore space and thus supporting the load. Due to lack of experimental data on the combined influence of alkali-metal cations (notably $\text{K}^+$ in the case of muscovite) and $\text{Al}^{3+}$ on dissolution rates in quartz, we cannot estimate the amount of decrease or increase in IPS rate the presence of both would cause.

Our results do not confirm the inference of Rutter & Wanten (2000) regarding the accelerating influence of phyllosilicates on pressure solution rate in quartz, nor the work of Hickman & Evans (1995) on the accelerating influence of clay films on pressure solution at halite/silica contacts. However, the pressure solution process at clay-free halite/silica and halite/halite contacts is diffusion controlled (Spiers et al., 1990), rather than interface controlled so that clay in grain boundaries can potentially increase pressure solution rates if it supports a thicker fluid film than in a clay-free boundary. Rutter & Wanten (2000) used an experimental set-up which included a separate reservoir of pure quartz sand as a (easy) sink for dissolved quartz. Precipitation is accordingly unlikely to become rate controlling in their experiments, and any decrease in precipitation rate caused by the presence of phyllosilicates would not be measured as a decrease in compaction rate. The increase of compaction rate that Rutter & Wanten (2000) reported, could perhaps have been caused by an increase in dissolution rate by the presence of alkali-metal cations (e.g., $\text{K}^+$, $\text{Na}^+$), released from the clay minerals and/or the muscovite. This is purely speculative, however, since doubt remains whether the increase in dissolution kinetics by alkali-metal cations is larger than the decrease caused by cations such as $\text{Al}^{3+}$ or $\text{Fe}^{3+}$. Alternatively, the enhancement of IPS reported by Rutter & Wanten (2000) could have been caused by a switch from precipitation or dissolution control in pure quartz sand to the parallel process of source-sink diffusion control in the sand-phyllosilicate samples with pure sand sink. Finally, Rutter & Wanten (2000) argue that the increase in IPS rates they observed may have been caused, in part, by the smaller total amount of quartz compared to the pure quartz samples and by additional compaction of the clay matrix by frictional and intracrystalline plastic processes, but these processes may have played a role in our experiments as well.

Clearly further systematic research is necessary to resolve the question of the effects of phyllosilicates on IPS in quartz. Nonetheless, our results have shown that muscovite causes no dramatic enhancement of IPS under condition favouring dissolution controlled IPS. IPS in nature may be diffusion controlled, especially since predictions of dissolution controlled IPS are too fast for low porosity sandstones. To assess if phyllosilicates have an accelerating effect in the diffusion-controlled field, experiments need to be conducted on coarse-grained samples and/or low porosity samples.
3.6. Conclusions

1. We have conducted 1-D compaction experiments on quartz-muscovite mixtures at a confining pressure of 300 MPa, a fluid pressure of 200 MPa, an effective pressure of 100 MPa and a temperature of 500 °C, in order to investigate the effect of muscovite on IPS rates in quartz sand. Under the chosen conditions dissolution controls the rate of IPS in pure quartz sand.

2. The presence of muscovite does not accelerate IPS rates in quartz sand under these conditions, but decreases compaction rates slightly, possibly due to a decrease in IPS rate.

3. If real, the effect of muscovite in slowing IPS may be due to the net effect of dissolved aluminium (Al\(^{3+}\)) decreasing the solubility, dissolution rate and precipitation rate of quartz.

4. The possibility that muscovite (and other phyllosilicates) strongly enhances grain boundary diffusion and hence IPS in quartz under laboratory or natural conditions favouring grain boundary diffusion control in pure quartz can not be eliminated on the basis of our experiments. To test if this occurs, experiments need to be performed on coarse quartz sand, lower porosities or using different pore fluid(s) (e.g. acidic fluids).

5. Enhanced IPS in nature and experiments could also be due to chemical effects on the precipitation and/or dissolution reactions, depending on the composition of the phyllosilicate and competing effects of alkali-metals vs. Al\(^{3+}\) or Fe\(^{3+}\). Experiments should be conducted on pure quartz sand with phyllosilicates of systematically varied influence on the composition of the pore fluid but not mixed with the sand.