

# Direct measurement of salt–mineral repulsion using atomic force microscopy

Andrea Hamilton,\* Vasileios Koutsos and Christopher Hall

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**The disjoining pressure between a mineral and soluble salt crystal in concentrated aqueous solution has been successfully measured with atomic force microscopy.**

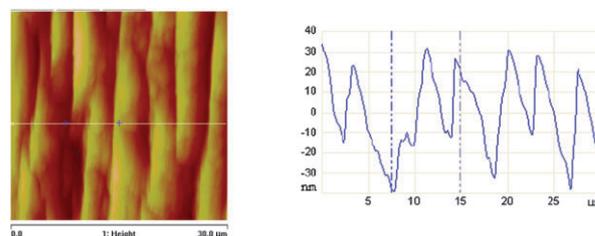
Salt crystals can grow in the pores of stone, generating stress in the host matrix and leading to serious damage<sup>1</sup> in building materials and works of art. Crystallization stress is also a cause of natural rock weathering in terrestrial and planetary landform alteration.<sup>2</sup> The ability of salt crystals to cause damage depends on the existence of a film of solution between the crystal and pore wall to allow continued growth, and a repulsive interaction between the crystal and the pore to maintain the film.<sup>3</sup> If the salt–mineral interaction through the film of solution is attractive, the salt crystal and pore wall make adhesive contact and no damage should be observed. The thickness of the solution film<sup>3</sup> is estimated to be a few nm, highlighting the importance of understanding and eventually tailoring the nanoscale interaction between salt crystals and rock forming minerals. The disjoining pressure is the force needed to push unit area of crystal and of pore wall into hard contact, and therefore is the upper bound on the real crystallization pressure. Our aim was to measure directly for the first time the disjoining pressure between a rock-forming mineral (using silica as an analogue for quartz) and a soluble salt crystal. Sodium sulfate, the most damaging<sup>2</sup> salt, has such complex hydrate chemistry<sup>4</sup> that force–distance AFM work was impractical. Therefore we used potassium sulfate (arcanite), chosen for its high solubility and its stability in air.

Potassium sulfate crystals were grown by evaporation on a freshly cleaved mica sheet to produce a smooth surface. Crystals were attached to the AFM stub with Araldite<sup>®</sup> 2014 and left to cure at room temperature in a desiccator for several weeks. We used a Multimode/Nanoscope IIIa (Veeco) AFM with a fluid cell. Room temperature was maintained at 21 °C. Heating from laser irradiation raises the temperature in the fluid cell by 3–4 °C.<sup>5</sup> Better surface stability was achieved by injecting solutions saturated at *ca.* 8 °C above room temperature with added crystal growth inhibitor. Potassium sulfate solutions saturated at 29 °C were used (0.595 M, Fisher AR grade, +99%), to which 5 ppm of Cr<sup>3+</sup> was added to the solution as KCr(SO<sub>4</sub>)<sub>2</sub>·12H<sub>2</sub>O (Sigma-Aldrich, ACS reagent grade, +99%).

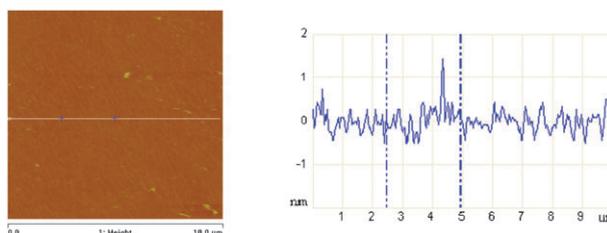
Solutions were injected through syringe filters (pore size 0.2 μm) to remove foreign particles. Custom-made CrAu

coated AFM cantilevers (Bioforce Nanosciences, USA) were designed with one standard imaging tip and a particle tip (5 μm silica) of nominal spring constants 0.12 and 0.58 N m<sup>-1</sup>, respectively, on the same side of the chip. The fluid cell and fittings were initially cleaned with a 2% solution of Micro-90 in an ultrasonic bath at 65 °C for at least 30 min. Cantilever, fluid cell and fittings were rinsed in deionized water (Millipore, 18.2 MΩ cm resistivity), ethanol, exposed to UV/ozone for at least 30 min and dried in a nitrogen stream. The spring constant of the particle tip was measured using the thermal noise method (1D MFP, Asylum Research).

Previous studies of potassium sulfate surfaces<sup>5</sup> have shown that the {0 2 1} faces always exhibit striations but these were found to be the largest faces and it was not possible to orient the much smaller but less striated faces in a workable way. Shown in Fig. 1 is a {0 2 1} surface imaged in K<sub>2</sub>SO<sub>4</sub> solution (no Cr<sup>3+</sup> added) which is obviously striated. We found we were able to suppress the striations by using Cr<sup>3+</sup> as a crystal growth inhibitor as shown in Fig. 2. The effect of templated growth against mica with addition of 5 ppm of Cr<sup>3+</sup> to the solution produces dramatic improvements in flatness. To check no residue of mica was present on the crystal surface, several templated arcanite crystals were etched slowly with



**Fig. 1** 30 × 30 μm scan of a templated arcanite surface in 0.595 M solution with no inhibitor. A section through the image is shown (left). Peak-to-trough max and RMS roughness are 115 nm and 20.9 nm respectively.



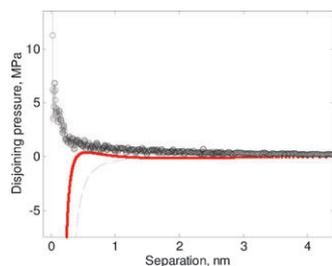
**Fig. 2** 10 × 10 μm scan of a templated arcanite surface in 0.595 M solution with 5 ppm Cr<sup>3+</sup>. A section through the image is shown (left). Peak-to-trough max and RMS roughness are 9.18 nm and 0.31 nm respectively.

School of Engineering and Centre for Materials Science & Engineering, The University of Edinburgh, The King's Buildings, Edinburgh, UK. E-mail: andrea.hamilton@ed.ac.uk; Fax: +44 (0)131-650-6554; Tel: +44 (0)131-650-5693

water under an optical microscope, and others imaged and mapped by SEM with EDX facility. Neither of the two crystals used for the data presented here contained any detectable trace of mica.

After imaging the surface, 4 mL of solution was flushed through the cell and 155 force curves were taken using the silica colloid cantilever at a piezo speed of 0.1 Hz. The raw tip deflection vs. piezo movement data were converted to force–separation curves using the measured spring constant and deflection sensitivity measured from the top part of the approach curve. The point of zero distance was determined as described by Butt *et al.*<sup>6</sup> by extrapolating between the contact region of the curve and the non-contact region at large separations. The resulting force–separation curves were averaged to produce a single curve which was smoothed using a 5-point FFT routine. The Derjaguin approximation is used to obtain the corresponding interaction free energy per unit area between two flat plates and the resulting curve differentiated to achieve the disjoining pressure vs. separation (Fig. 3).

It is clear that no obvious minima, primary or secondary, are observed and that the interaction is essentially repulsive at all separations. Modeling the system using the algorithm of Chan<sup>7</sup> which solves numerically the non-linear Poisson–Boltzmann equation for asymmetrical electrolytes but modified to include dissimilar surfaces and van der Waals interactions predicts an attraction beginning at 0.5–1.5 nm (see Fig. 3). Modification for dissimilar surfaces was achieved by integrating twice for  $\kappa L$  (inverse Debye length multiplied by surface separation  $L$ ), with the lower limit of integration being the potential minimum in both cases, but the upper limits set at the surface potential for the two dissimilar surfaces. The total  $\kappa L$  value is the sum of the two  $\kappa L$  values which together equal the dimensionless distance between the plates. van der Waals forces are calculated for a sphere and a plane and converted to pressure *via* the Derjaguin approximation and differentiating the equation for interaction free energy per unit area.<sup>8</sup> The Hamaker constant used is calculated for arcanite/silica–potassium sulfate solution using the Lifshitz approximation; retardation effects are not considered. Modeling was carried out for constant potential and constant charge, as shown in Fig. 3, which are generally considered the standard lower and upper boundaries, respectively, in DLVO theory. What is clear from the fit is that DLVO does not adequately describe either the length scale or the nature of the interaction at short distances but that constant charge (CC) is a slightly better fit than constant potential (CP). Bostrom *et al.*<sup>9</sup> state that at



**Fig. 3** Disjoining pressure calculated from smoothed average of 155 force curves (black circles). DLVO CP fit (dashed line) and CC fit (dotted line).

concentrations above 0.1 M DLVO theory is flawed and describe a method for taking the image and dispersion forces between ions into account. The result is a stronger attraction than that predicted by DLVO (constant potential) which does not describe the results presented here. An approximation to the shape of the curve, up to gap length of *ca.* 0.5 nm, can be obtained with the constant charge boundary condition at surface potentials of  $-22$  mV and  $-19$  mV for silica and arcanite (Fig. 3). Reducing the input surface potential to much lower values in both the CC and CP models produces a primary minimum with little or no repulsion visible at any separation. This is not surprising since at high salt concentrations the charge and potential generally tend towards zero and the electrostatic part of DLVO is screened out leaving the vdW contribution only. In salt crystallization damage in rocks, crystal growth must occur in concentrated supersaturated solution with little or no electrostatic component. This suggests the repulsive regime observed here applies to other salt–mineral systems for which crystallization damage is observed.

Very little literature exists on surface interactions in concentrated ( $>0.1$  M) solution and even less on dissimilar surfaces. Long range hydration repulsion, extending out to 7 nm, between mica sheets at high NaCl concentration (60–600 mM) was observed by Alcantar *et al.*,<sup>10</sup> who remarked that hydrated  $\text{Na}^+$  could push apart mica sheets forced together under 10–50 MPa of pressure by up to 3 nm. They attribute this long range interaction to hydrated  $\text{Na}^+$  binding to negative sites on the mica surface. Work on silica<sup>11,12</sup> shows that less hydrated ions such as  $\text{K}^+$  and  $\text{Cs}^+$  bind more easily to the silica surface and that at high concentrations ( $\sim 1$  M)  $\text{K}^+$  ions condensed on the surface can produce a surface charge inversion. In the case of charge inversion, they describe an extra short-range repulsion that takes place at separations  $<2$  nm (0.5 M CsCl) after a pronounced vdW attraction and describe it as a short range electrical double layer repulsion. Ion and surface specific effects and long range non-DLVO forces are also evident in the force–distance experiments of Veeramasuneni *et al.*<sup>13</sup> using a silica colloid tip and NaCl and KCl crystals in saturated solution. With NaCl they find a strong attraction extending to  $\sim 17$  nm and with KCl a purely repulsive interaction to  $\sim 4$  nm. Although they do not calculate disjoining pressure for either system their results suggest KCl has the potential to be damaging to siliceous stones where NaCl is not. Ion and crystal face specific interactions are described by Finot *et al.*,<sup>14</sup> who measured forces between silica and gypsum and pairs of gypsum crystals in solutions an order of magnitude less concentrated than the solutions used here.

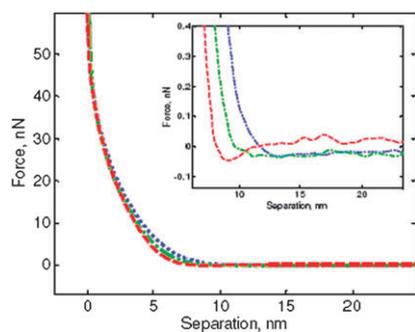
Our results show a long range repulsion, consistent with that of Alcantar *et al.*,<sup>10</sup> and no strong attraction. A very slight secondary minimum (not shown) is found at *ca.* 13 nm with a force value of 32 pN followed by a substantial repulsion and no observable primary minimum.  $\zeta$ -Potential measurements were made (Malvern, Zetasizer Nanoseries) on particles of arcanite (not more than 10  $\mu\text{m}$  in diameter) and silica (Aston Chemicals UK, 3  $\mu\text{m}$  diameter, 50  $\text{\AA}$  pore size) in 0.595 M  $\text{K}_2\text{SO}_4$  with 5 ppm  $\text{Cr}^{3+}$  which suggested a near zero but slightly negative  $\zeta$ -potential for both particles. As the diffuse

double layer shrinks, the  $\zeta$ -potential tends towards zero but the standard deviation, which is  $\pm 3$ – $4$  mV means that the absolute value is a rough guide. The high solubility of arcanite crystals makes it impossible to measure the  $\zeta$ -potential in dilute solution, which would be more consistent with standard practice. The effect of adding 5 ppm  $\text{Cr}^{3+}$  to maintain arcanite surface stability was investigated through  $\zeta$ -potential measurements on silica spheres in 0.6 and 6 mM  $\text{K}_2\text{SO}_4$  solutions with and without 5 ppm  $\text{Cr}^{3+}$ . Results were  $-25.6$  mV (0.6 mM, no  $\text{Cr}^{3+}$ ),  $-26.5$  (0.6 mM, 5 ppm  $\text{Cr}^{3+}$ ),  $-7.0$  mV (6 mM, no  $\text{Cr}^{3+}$ ) and  $-7.3$  mV (6 mM, 5 ppm  $\text{Cr}^{3+}$ ) which are consistent with the fact that the Debye length is not affected by the addition of 5 ppm  $\text{Cr}^{3+}$ .

When the experimental curve in Fig. 3 is fitted to a second order exponential, we obtain values of 2.3–2.7 MPa for the disjoining pressure at 0.165–0.2 nm.<sup>10</sup> The decay length of the repulsion is 2.9 nm, an order of magnitude higher than the Debye length but fairly consistent with the non-DLVO repulsion observed by Alcantar *et al.*,<sup>10</sup> who report a decay length of 1 nm. Beyond the repulsion, hard contact is reached. Although a primary minimum is not observed, an adhesion force is measured on retraction. Calculating<sup>15</sup> the pull-off force from measured surface roughness and the estimated van der Waals force gives a value about 25 times greater than the measured pull-off force. This suggests that either the surface roughness is much higher in the area sampled by the colloid tip or that even at hard contact, repulsive non-DLVO forces effectively reduce the tip-sample adhesion.

An ultimate aim of studying the disjoining pressure is to find a method of tailoring the interaction at small separations to promote an attractive interaction and reduce damage from salt crystallization. Zohar *et al.*<sup>16</sup> find charge inversion between silica surfaces in the presence of  $Z = 3$  ions which dramatically alters their force curves from a long range repulsion to a much shorter range attraction. To see if this can occur in silica/arcanite, saturated potassium sulfate solutions were prepared at 29 °C with 5, 50 and 500 ppm of crystal growth inhibitor. An equilibration time of 15 min was allowed before force curves were captured. At least 4 mL of each new solution was flushed through the cell prior to data collection. 155, 47 and 50 force curves were analyzed for the 5, 50 and 500 ppm solutions respectively.

Fig. 4 shows a typical set of force–separation curves with additions of 5, 50 and 500 ppm inhibitor  $\text{Cr}^{3+}$ . It is clear that



**Fig. 4** Force–separation curves for the three solutions of 0.595 M potassium sulfate containing 5 ppm (dotted line), 50 ppm (dot-dash line) and 500 ppm (dashed line) of  $\text{Cr}^{3+}$ .

at 500 ppm, an attraction appears on approach at *ca.* 9 nm but that it is still followed by repulsion. The Debye length changes very little on addition of 500 ppm  $\text{Cr}^{3+}$  but  $\zeta$ -potential measurements suggest that surface charge inversion by 500 ppm of  $\text{Cr}^{3+}$  is more effective than predicted charge inversion from very high concentrations of monovalent cations,<sup>16</sup> 1.19 M  $\text{K}^+$  in this case.  $\zeta$ -Potential values for silica spheres in 0.6 mM  $\text{K}_2\text{SO}_4$  with 5, 50 and 500 ppm added are  $-26.5$ ,  $-24.2$  and  $-19.2$  mV respectively. For 6 mM  $\text{K}_2\text{SO}_4$  with 5, 50 and 500 ppm  $\text{Cr}^{3+}$  added the  $\zeta$ -potential results are  $-7.3$ ,  $-4.7$  and  $-1.4$  mV respectively. At 500 ppm  $\text{Cr}^{3+}$  6 out of the 11 samples analyzed had positive values under  $+3$  mV but again a standard deviation of  $\pm 3$ – $4$  mV per measurement. While the absolute value of samples at close to 0 mV cannot be taken too literally, the trend towards charge inversion is clear. Analysis of arcanite crystals in 0.595 M  $\text{K}_2\text{SO}_4$  solutions with the same set of  $\text{Cr}^{3+}$  additions also suggests the surface could be positively charged in 500 ppm  $\text{Cr}^{3+}$ . Ion correlation effects (vdW forces between polarisable counterions) are responsible for the attraction at *ca.* 9 nm and the repulsion at shorter range suggests  $\text{Cr}^{3+}$  is not tightly bound to the surface. The use of  $\text{Cr}^{3+}$  shows that it is possible to tailor salt–mineral interactions, for example through charge inversion. This opens a possible important new approach to prevent salt crystallization damage in building materials.

Results from a total of 455 measurements on two crystals at  $\text{Cr}^{3+}$  concentrations of 5, 50 and 500 ppm were analysed to arrive at a disjoining pressure for silica–arcanite in potassium sulfate solution of 2.4 to 4 MPa. This is at the lower end of the range (*ca.* 2–9 MPa) of tensile strength for most sedimentary rocks<sup>17</sup> and may explain damage through slow crack propagation in cyclical crystallization tests. Charge inversion by  $\text{Cr}^{3+}$  produces an attraction at long range between silica and arcanite with repulsion at short range. This is the first measurement of disjoining pressure and charge inversion in a salt–mineral system and proof that a repulsive interaction can exist between minerals and salt crystals in salt solution.

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