Experimental investigation of the mechanical properties of synthetic magnesium sulfate hydrates: Implications for the strength of hydrated deposits on Mars

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[1] We have carried out uniaxial compression experiments to determine the mechanical properties of three crystalline magnesium sulfate hydrates that may be present in the near-surface environment of Mars. Our synthetic samples of kieserite (MgSO4 · H2O), epsomite (MgSO4 · 7H2O), and meridianiite (MgSO4 · 11H2O) have mean values of unconfined compressive strength of 6.3 ± 0.7, 12.9 ± 1.8, and 30.1 ± 4.5 MPa, respectively, Young’s modulus of 0.8 ± 0.1, 2.9 ± 0.4, and 5.9 ± 0.8 GPa, respectively, and mean porosity values of 47.8% ± 0.5%, 11.1% ± 0.6%, and 2.9% ± 0.2%, respectively. Although our tests cannot quantify a systematic relationship between hydration state and mechanical properties, the different porosities produced by consistent sample preparation methods suggest that the addition of non-cation-coordinated water molecules likely reduces the strength of individual sulfate hydrate phases. However, the bulk mechanical properties of our synthetic specimens are instead controlled predominantly by the sample porosity; generally, the strength increases as the porosity decreases. We expect the mechanical properties of sulfate hydrate deposits on Mars to be governed by the bulk porosity rather than the strength of the pure solid phase. We have performed cyclic stressing tests, replicating possible periodic depositional and erosional periods on Mars resulting from obliquity changes. A gradual compaction and reduction in sample porosity, rather than an increase in crack damage, is observed with each loading cycle, suggesting that the evolution of mechanical properties will depend on local factors such as bulk density, in addition to the overall stress history.


1. Introduction

[2] The present stable phase of water on Mars is in the form of ice. Large volumes of water ice exist permanently in the northern [Kieffer et al., 1976] and southern [Titus et al., 2003] polar ice caps, which extend poleward from latitudes of 80° [e.g., Clifford et al., 2000]. Subsurface ice is likely at lower latitudes [Boynton et al., 2002], with theoretical studies of permafrost stability predicting that ice may be stable even in near-equatorial regions during periods of high obliquity [Mellon et al., 1997]. Neutron and gamma-ray spectroscopy has revealed hydrogen-rich near-surface (<1 m) soil that generally correlates with the predicted stability of water ice [Feldman et al., 2004], indicating an average subsurface layer that may be ~60% ice by volume [Boynton et al., 2002]. There is also indirect mineralogical evidence of water: the iron oxide hematite (Fe2O3), which often forms in standing water, has been identified from orbit by the Thermal Emission Spectrometer onboard Mars Global Surveyor [Christensen et al., 2000] and the Observatoire pour la Mineralogie, l’Eau, les Glaces et l’Activité (OMEGA) instrument onboard Mars Express [Gendrin et al., 2005]. The presence, and likely water-borne formation, of hematite was recently confirmed in situ by the Mars Exploration Rover Opportunity in Meridiani Planum [e.g., Squyres et al., 2004].

[3] However, a considerable volume of water is probably also locked up in a range of crystalline hydrates, which are important water reservoirs where ice is not stable at the surface. Orbital observations at near-infrared wavelengths...
have revealed an abundance of hydrated sulfate minerals. OMEGA has identified hydrated minerals, including gypsum (CaSO₄ · 2H₂O), kieserite (MgSO₄ · H₂O), epsomite (MgSO₄ · 7H₂O), and some Fe sulfates at a range of latitudes [Gendrin et al., 2005; Horgan et al., 2009]. These deposits are most common in canyons in Valles Marineris, often in association with light-toned deposits [Gendrin et al., 2005]. Recent high spatial resolution observations by the Compact Reconnaissance Imaging Spectrometer for Mars (CRISM) have confirmed the association of sulfate hydrates with light-toned layered deposits [e.g., Bishop et al., 2008; Lichtenberg et al., 2008]. In some cases, these layered deposits are several hundred meters thick [Roach et al., 2008], and although water is a requirement for formation, the exact nature of the water (e.g., atmospheric, standing, transient) during formation, and hence the timing in relation to the formation of Valles Marineris, is a matter of ongoing debate [e.g., Chapman and Tanaka, 2001; Komatsu et al., 2004; Catling et al., 2006; Mangold et al., 2008; Okubo et al., 2008]. In situ evidence from rover observations also suggest the presence of hydrated magnesium sulfate minerals [Squyres et al., 2004], such as kieserite, epsomite, and meridianiite (MgSO₄ · 11H₂O) [Peterson and Wang, 2006], which are capable of repeat hydration cycles under present-day martian conditions [Chou and Seal, 2007], although metastability and irreversible kinetic pathways might be important for some of the phase changes [e.g., Vaniman and Chipera, 2006; Chipera and Vaniman, 2007; Wang et al., 2009].

Determining the location and role of water on Mars today, and its effects over geological time, requires a proper understanding of both the thermodynamic and the mechanical stability of sulfate hydrates under martian conditions. The mechanical properties of these hydrates are of importance because they may be involved in controlling the stability of slopes and canyon walls. Here we address the mechanical properties of magnesium sulfate hydrates by using well-validated experimental rock physics techniques. Specifically, we aim to determine the drained unconfined compressive strength (UCS or σc), Young’s modulus (E), and Poisson’s ratio (ν) of martian sulfate analogs as these are key parameters in governing the strength and deformability of similar deposits on Mars [e.g., Okubo, 2007]. The goal of this study is twofold: (1) to determine the mechanical properties of sulfate hydrates in general to better understand their mechanical stability on Mars and (2) to quantify any relationship between hydration state and mechanical deformation with a length-to-diameter ratio of 3:1 (75 mm long by 25 mm diameter) [Mogi, 1966; Hawkes and Mellor, 1970] by packing these powders into a split die assembly and pressing to ~150 MPa. Samples were precision-lathed before deformation to ensure flat- and parallel-loading faces.

For each hydride phase, we checked the purity of a representative sample using X-ray diffraction analysis on a PANalytical X’Pert Pro powder diffractometer (Co Kα radiation). The MS7 powder was supplied as 99% pure and, after powdering, packing, and lathing, exhibited no discernible change in bulk composition. The MS1.25 sample was supplied as nominally 97% pure MgSO₄ · H₂O. However, the bulk composition of this material seems to correspond to that of the poorly characterized hydrate of MgSO₄ · 1H₂O; also, in material scraped from the surface of our prepared kieserite cylinder, we detected the onset of formation of higher hydrates. As shown in Figure 1a, the X-ray powder diffraction patterns of the surface scraping contains numerous sharp Bragg reflections, which, in both position and intensity, agree with the expected diffraction pattern of sanderite (MgSO₄ · 2H₂O) [Ma et al., 2009]. The remaining observed Bragg reflections match well with those reported from the poorly known MgSO₄ · 1.25H₂O phase, which has been previously referred to as “synthetic kieserite” [Emons et al., 1990]. On the basis of these X-ray diffraction data, it appears that no (or very little) kieserite [Aleksosvka et al., 1998] is present. In particular, the single broad feature at ~2θ = 32° in our X-ray powder diffraction pattern cannot be explained by kieserite, but instead, this closely matches two close Bragg peaks in the 1.25 hydrate. Consequently, we checked the exact water content of the MS1 starting material as supplied by Sigma-Aldrich using a thermogravimetric method, similar to that of Emons et al. [1990]. We heated a small (~5 g) sample of the supplied MS1 to 400°C for 24 hours and measured a mass reduction of 16.9%; the water contents of MgSO₄ · H₂O, MgSO₄ · 1.25H₂O, and MgSO₄ · 2H₂O are 13.0%, 15.8%, and 23.0%, respectively. Therefore, it is likely that our supplied MS1 contains a large proportion of MgSO₄ · 1.25H₂O, which, although having no significant effect on our results (see discussion on porosity below), does...
mean that we prefer to use the term MS1.25 throughout this paper when referring to this sample.

[7] In the case of X-ray diffraction analysis of MS11, we constructed a small cold stage using a Peltier cooler and aluminum alloy radiator coupled to a sample stage enclosed in an X-ray transparent polyester film; this allowed us to maintain a sufficiently low temperature to prevent incongruent melting of MS11 at 2°C and to limit the availability of atmospheric moisture that could condense on the specimen. The version of the cold stage used for this experiment was a prototype in which the sample was imperfectly sealed from the atmosphere in the laboratory; consequently, we found that a highly oriented film of water-ice grew rapidly on the exposed MS11 surface. We performed a series of rapid (~4 min) scans over the angular range = 25°–35° that allowed us to observe the growth of the ice film and so determine the purity of the original sample (at time \( t = 0 \)).

Figure 1b shows the first diffraction pattern: very weak Bragg reflections from ice (red tic marks) are present. Rietveld refinement yields an ice abundance of 1.5 wt% after 4 min, growing to 55 wt% after 50 min. Extrapolating backward to time \( t = 0 \) using the equation of Avrami [1939] (Figure 1c) shows that our quenched specimens are initially ice free. The value of the Avrami exponent, \( n = 1.9 \) (Figure 1c) is indicative of platy (i.e., two-dimensional) interfacial growth on a substrate that is saturated in nucleation sites, for which we would expect \( n = 2 \). Clearly, quenching of stoichiometric liquid in liquid nitrogen yields the equilibrium phase and does not result in disproportionation to a mixture of MS7 + ice.

[8] Measuring the porosity of our magnesium sulfate samples is nontrivial because most methods involve either the destruction of a sample or the use of a saturating (and, in this case, dissolving) fluid. Therefore, we sought to measure the porosity using nondestructive methods. The total porosity of each sample was determined using a relative density method by comparing the sample density, measured with digital calipers and mass balance, with that of the pure hydrate phase; the precision of our total porosity measurements is high (absolute maximum probable error <2% for all samples). We also used two additional methods of measuring porosity on representative samples: (1) saturation in silicone oil and (2) gas pycnometry. By comparing the results from the three different analytical techniques, we can determine the proportion of isolated and connected pores.

[9] We measured the effective (connected) porosity of samples of MS1.25 and MS7 by vacuum-driven saturation in silicone oil at room temperature. We used silicone oil as the saturation medium rather than water because of the high solubility of magnesium sulfate hydrates in water. The dry mass of each sample was recorded before the sample was left to saturate for several hours in the silicone oil, immediately after which the wet mass was recorded. The relative mass increase allowed the effective porosity to be determined. Our saturated samples of MS1.25 and MS7, which were not used in deformation tests, have total porosities of 49.3% and 6.4%, respectively, compared with effective porosities of 19.4% and 2.2%, respectively, yielding total-to-effective porosity ratios of 2.5 and 2.9, respectively. These ratios are toward the upper range found in natural evaporates [e.g., Bell, 2000], indicating that our sample
preparation method is efficient at isolating pores but not necessarily at closing them.

[10] This difference in total and effective porosity is not surprising because we would expect the effective porosity to be less than the total porosity because saturation penetrates only those pores connected to the surface and does not reflect the porosity of the bulk sample. There is a possibility that the low connected porosity is the result of using silicone oil rather than water. Using the equation of Washburn [1921], we estimate that, although the minimum pore size that silicone oil can penetrate is approximately four times the diameter of the pores accessible to water, it is still in the submicrometer range. This minimum pore size can be compared with pores visible in a scanning electron microscope (SEM) analysis of another representative MS1.25 sample (Figures 2a and 2b). At this resolution, individual grains and pores are visible and do not appear to have any preferred orientation. Individual pores less than ∼10 μm are evident as gaps between grains and, in a few cases, join together to form connected pore networks. From these SEM images on an undeformed sample, it is not possible to quantitatively determine the exact porosity, although it is evident that there appears to be no preferred pore orientation.

[11] We also measured the total porosity of the same MS1.25 sample used in the SEM analysis using gas pycnometry. We used a Micromeritics AccuPyc 1330 helium pycnometer on a sample lathed down to an apparent volume of 0.862 cm³ (maximum standard error ∼15%). We measured the mean true volume and specific gravity of the sample to be 0.4155 cm³ and 2.5782, respectively, from 10 individual analyses in the pycnometer, giving one SD precision errors of <0.4% in both cases. This yielded a porosity value from pycnometry (51.8% ± 0.3%) comparable with that measured through density analysis (mean porosity = 49.0% ± 0.2%). Because helium is highly penetrating, we would expect the results from helium pycnometry to be in good agreement with the total porosity determined from the relative density, and this is indeed the case.

[12] It is also necessary to determine the effects on our porosity measurements of our supplied MS1 most likely being dominated by MS1.25. Because the structure of MgSO₄ · 1.25H₂O is yet to be solved, the exact density of this phase is also unknown. However, if the density of the 1.25 hydrate lies proportionally between that of the monohydrate (2570 kg m⁻³) and the dihydrate (2370 kg m⁻³), we can estimate the density of “synthetic kieserite” as 2520 kg m⁻³. This change in pure phase density would result in a decrease
in our calculated porosities of 1% for all our MS1 samples. Because the density of MS1.25 above is an estimate because of its structure being unsolved, we use the known density of MgSO$_4$·H$_2$O in calculating the porosity of MS1.25 throughout. Therefore, we are confident that our relative density porosity measurements for representative samples compare well with those from alternative methods and that our porosity values for all samples used in our deformation experiments are accurate.

3. Experimental Procedure

We applied well-validated experimental rock physics techniques, used in the study of terrestrial volcanic samples and systems [e.g., Bredthauer, 1957; Murrell and Chakravarty, 1973; Rohde and Feng, 1990; Schultz, 1993, 1995; Rocchi et al., 2002; Heap et al., 2009], to our synthetic magnesium sulfate hydrates. We used a servo-controlled 200 kN uniaxial load frame (Figure 3), with an environmental chamber capable of temperatures of between −150°C and 350°C, to conduct unconfined compression tests. Using the signal from an external linear voltage displacement transducer, we deformed samples at a constant axial strain rate while monitoring the resultant axial and radial strains. We also recorded acoustic emission (AE) energy, a proxy for crack damage, over the range 0.1–1 MHz using a MISTRAS-2001 system with broadband piezoelectric transducers located inside the top and bottom loading anvils [Cox and Meredith, 1993]. Each sample was sealed from the environment during deformation by a thin (~10 μm) layer of low-density polyethylene, which prevented possible humidity-related phase changes without affecting sample strength or radial strain measurements.

[14] We carried out two main types of constant strain rate tests: (1) compression-to-failure to determine UCS ($\sigma_c$) and static elastic moduli, Young’s modulus ($E$), and Poisson’s ratio ($\nu$), during a single loading cycle, and (2) cyclic stressing tests with incrementally increasing load to determine the evolution of elastic moduli with increasing crack damage. Strictly, our calculated values are the static elastic moduli, as opposed to the dynamic elastic moduli determined from elastic wave velocities. In both types of compression tests, our values of UCS are the maximum stresses recorded before sample failure, whether in a brittle or in a ductile manner. We obtained static elastic moduli during the quasielastic (linear) portion of a load cycle. The Young’s modulus, or tangent modulus [e.g., International Society of Rock Mechanics, 1978; Jaeger et al., 2007], was calculated using the local gradient of a third-order polynomial fitted to the stress-strain curve [Faulkner et al., 2006; Heap and Faulkner, 2008], and this is given by

$$E = \frac{\partial \sigma}{\partial \varepsilon_{\text{axial}}}$$

(1)

with a similar approach used to determine Poisson’s ratio given by

$$\nu = -\frac{\partial \varepsilon_{\text{radial}}}{\partial \varepsilon_{\text{axial}}}$$

(2)

where $\sigma$ is the applied longitudinal stress and $\varepsilon_{\text{axial}}$ and $\varepsilon_{\text{radial}}$ are the axial and radial strains, respectively. In cyclic stressing tests, we repeatedly loaded and unloaded the sample at a constant strain rate, increasing the maximum load at each cycle while always unloading to a similar minimum stress in each test. These tests allowed us to quantify the evolution of static elastic moduli with pore collapse and/or increasing crack damage.

4. Results

[15] We have carried out 35 uniaxial compression tests, with 12 on MS1.25, 11 on MS7, and 12 on MS11. We used controlling strain rates of between $1.2 \times 10^{-4}$ and $6.8 \times 10^{-7}$ s$^{-1}$ and environmental temperatures between 223 and 323 K. Of these tests, 32 were single compression-to-failure tests and 3 were cyclic stressing tests. All results are given in Table 1, and described below in more detail.

4.1. Compression-to-Failure Tests

Representative results from single-loading failure tests, showing loading path and AE energy, are shown in Figure 4. In these examples, samples of MS1.25, MS7, and MS11 failed at 6.4, 9.4, and 75.0 MPa at temperatures of...
248, 248, and 223 K, respectively. Samples demonstrating higher UCS also yielded a greater AE energy. Although we do not specifically address postfailure behavior in this study, we do note that of the 32 single-compression-to-failure tests, 28 resulted in failure in a gross brittle manner, with a sudden marked decrease in stress and usually significant, if not complete, axial fracturing on failure. Four tests on MS11 (runs 1, 2, 3, and 5) resulted in ductile failure, with little or no axial fracturing, and a gradual loss in strength after peak stress had been achieved (Figure 5). As a system, our magnesium sulfate hydrates have UCS values between 4.3 and 75.0 MPa across the temperature range studied. Individually, MS1.25, MS7, and MS11 have mean UCS values of \( 6.3 \pm 0.7 \) MPa (range = 4.3–10.0 MPa), \( 12.9 \pm 1.8 \) MPa (range = 6.3–21.2 MPa), and \( 30.1 \pm 4.5 \) MPa (range = 13.5–75.0 MPa), respectively. Test temperature seems to exert little influence on the UCS and elastic moduli of our samples, except for tests on MS11 close to its incongruent melting temperature, and hence undergoing ductile deformation, which failed at lower stress. Our MS1.25 samples showed sufficient range in porosity to demonstrate that porosity is the dominant parameter in determining the mechanical properties of our samples (Figure 6), the justification of which we discuss in section 5.1, and allows us to consider the magnesium sulfate system as a whole.

Our samples of MS1.25, MS7, and MS11 have mean porosity values of \( 47.8\% \pm 0.5\% \), \( 11.1\% \pm 0.6\% \), and \( 2.9\% \pm 0.2\% \), respectively, showing a negative trend with UCS. We describe this trend using the theoretical approach of Phani and Nyvigt [1987] for describing Young’s modulus as a function of porosity in porous brittle solids, where the UCS is given by

\[
\sigma_c = \sigma_0 (1 - \phi / \phi_c)_Y
\]

where \( \sigma_0 \) is the UCS at zero porosity, \( \phi \) is the porosity, \( \phi_c \) is the critical porosity at which UCS is zero, and \( f_3 \) is an exponential factor. Here we assume that UCS will be 0 when porosity is equal to 1, when a sample would effectively contain no solid components. The values of the parameters obtained by fitting the data shown in Figure 7a to equation (3) are given in Table 2, the fit is shown in Figure 7a by a solid line (coefficient of determination, \( R^2 = 0.54 \)). Reducing \( \phi_c \) to 0.5 reduces \( f_3 \) by roughly a similar amount (–41%), but has little effect on \( \sigma_0 \) and \( R^2 \).

The elastic moduli of magnesium sulfate hydrates show a similar porosity-dominated trend to that of their UCS. The Young’s modulus determined from single loading tests ranged between 0.5 and 10.5 GPa. Different phases show significant variation in Young’s modulus, with
MS1.25, MS7, and MS11 having mean Young’s modulus values of 0.8 ± 0.1 GPa (range = 0.5–1.5 GPa), 2.9 ± 0.4 GPa (range = 0.5–5.5 GPa), and 5.9 ± 0.8 GPa (range = 2.3–10.5 GPa). The Young’s modulus of the samples again showed a negative trend with increasing porosity (Figure 7b), which we describe using the theoretical approach of Phani and Niyogi [1987], in which the Young’s modulus is given by

\[
E = E_0 (1 - \phi / \phi_c)^{\delta}
\]

(4)

where \(E_0\) is the Young’s modulus at zero porosity, \(\phi_c\) is the critical porosity at which Young’s modulus is 0, and \(\delta\) is an exponential factor. We assume that Young’s modulus will be zero when there are no solid components in the sample, effectively setting the critical porosity to one. The values of the parameters obtained by fitting the data shown in Figure 7b to equation (4) are given in Table 3; they produce the best fit plot \((R^2 = 0.63)\) shown by the solid line in Figure 7b. Reducing \(\phi_c\) to 0.5 reduces \(\delta\) by roughly a similar amount (≈43%), but this has little effect on \(E_0\) and \(R^2\).

Determining Poisson’s ratio in our tests proved problematic; movement of the radial linear voltage displacement transducer owing to either air movement from the environmental chamber fan or ice buildup during long duration cold runs meant that the Poisson’s ratio could only be determined in seven of our compression-to-failure tests. Of these seven successful tests, two were on MS1.25, four on MS7, and one on MS11. The mean Poisson’s ratio in these tests ranged from 0.06 to 0.24, with the greatest range observed for MS1.25 samples, which had the highest porosities. During each test, the instantaneous value of Poisson’s ratio increased with stress, indicating crack damage and/or pore closure. Poisson’s ratio is the major factor in determining the Poisson’s ratio of a sample, which showed an increasing trend with increasing porosity (Figure 7c), which we describe using two different methods. First, we adopt the approach of Phani and Sanyal [2005] and assume that the pores in the samples are spherical so that Poisson’s ratio can be given by

\[
\nu = 0.5 - \frac{3(1 - 2\nu_0)(1 - \phi^2)}{6[(a_5\phi + b_5)K_{p,1} + (c_5\phi + d_5)K_{p,2}]}
\]

(5)

where \(\nu\) is the Poisson’s ratio at zero porosity, \(a_5, b_5, c_5, d_5,\) and \(K_{p,1}\) and \(K_{p,2}\) are polynomial parameters related to

Figure 4. Representative results from single compression-to-failure tests for (a) MS1.25, (b) MS7, and (c) MS11. In each case, the run number, temperature, and strain rate are given in addition to the stress (solid blue line) and AE (solid red line) as a function of time. Jumps in cumulative energy correspond with stress drops (black arrows), indicating that cracking of the sample is associated with release of acoustic energy [e.g., Tuffen et al., 2008]. The UCS values for these three samples of (a) MS1.25, (b) MS7, and (c) MS11 are 6.4, 9.5, and 75.0 MPa, respectively.

Figure 5. Brittle versus ductile failure mechanisms in MS11. Brittle failure in MS11 run 4 (solid black line) at \(T = 248\) K is evident from the sudden loss of strength after peak stress at 28.2 MPa. Ductile failure in MS11 run 3 (solid gray line) at \(T = 261\) K can still accommodate significant amounts of strain after failure at 16.9 MPa.
Mechanical properties of our MS1.25 samples as a function of porosity, which allows us to separate the effect of composition from the sample porosity. (a) UCS and (b) Young’s modulus of all our tests on MS1.25 as a function of sample porosity demonstrating that an increase in porosity causes a decrease in overall strength. The fill colors represent the test temperatures as given in the scale bar. The white lines on the temperature scale represent the test temperatures of 233, 248, 300, and 323 K. Porosity error bars are the maximum probable error, and vertical error bars are one SD for each experiment.

Young’s modulus. The values of the parameters obtained from fitting equation (5) are given in Table 4; they produce the best fit plot ($R^2 = 0.76$) shown by the broken line in Figure 7c. Second, for simplicity, we also fit an exponential curve for comparison with the theoretical fit, where Poisson’s ratio is given by

$$\nu = 0.5 - a_6 \exp(b_6/\phi)$$

where the values of the fitted parameters $a_6$ and $b_6$ are given in Table 4 and used to produce the best fit plot ($R^2 = 0.77$) shown by the solid line in Figure 7c.

4.2. Cyclic-Stressing Tests

Representative results from a single cyclic-stressing test are shown in Figure 8. In this test, the MS7 sample was loaded and unloaded at a constant strain rate of $1.7 \times 10^{-6} \text{s}^{-1}$, at a temperature of 300 K, yielding a UCS of 20.3 MPa (Figure 8a). This single experiment lasted for more than 7 hours and, at the given strain rate, enabled the sample to undergo eight complete cycles, failing during the loading portion of the ninth cycle. Figure 8b shows the corresponding stress-strain curve for this test and highlights the variation in the stress-strain response of the sample between loading cycles. To aid comparison between samples, all three cyclic-stressing tests were carried out under similar conditions, with a temperature of 300 K, and strain rates between $1.7 \times 10^{-6}$ and $3.6 \times 10^{-6} \text{s}^{-1}$. The measured values of static elastic moduli in our cyclic tests are also controlled by sample porosity and show significant evolution throughout testing (Figure 9). In each test, the mean value of $E$, measured over the quasielastic region of each cycle, increases with increasing cycle number (Figure 9a). In the one cyclic test in which we were able to confidently determine the Poisson’s ratio, MS7 run 8 (Figure 9b), increasing the number of stress cycles increased the Poisson’s ratio from 0.02 to 0.35, indicating significant microcrack damage during inelastic deformation.

5. Discussion

5.1. Interpreting the Experimental Results

To apply the experimental results to similar deposits on Mars, it is necessary to first recognize any possible limitations of the experimental procedure and to properly understand the processes occurring during deformation testing. The porosity of our samples is inherited from the sample preparation methods and is similar to those used in other studies of synthetic sulfate hydrate samples produced by packing; for example, de Meer and Spiers [1995] produced synthetic samples of gypsum for hydrostatic compression testing by compacting dry powders of grain size between 37 and 125 $\mu$m, resulting in porosities of 45% ± 3%. The process of compaction of dry powders can be split into four main stages: (1) first granular reorganization, (2) fragmentation, (3) second granular reorganization, and (4) plastic deformation and intermolecular bonding [Lamy et al., 2005]. The porosity variation between the different hydrate phases investigated in this study is most likely the result of different amounts of grain crushing during the fragmentation stage of sample preparation and, therefore, suggests some hydration state-strength relationship. All powders were sieved to a similar grain size and so likely underwent similar amounts of initial granular reorganization on compaction.

The presence of non-cation-coordinated water molecules, as found in the higher hydrates, likely reduces the bulk strength of sulfate hydrates, resulting in increased grain crushing during compaction, and hence a lower porosity, with increasing hydration state. In essence, the strongest individual grains produce the weakest samples through compaction. This process helps to explain our apparent paradoxical finding that the lowest hydrate in our study, MS1.25, was the weakest and justifies our interpretation that porosity is the governing factor in determining the bulk sample strength.
Position and porosity is probably indicative of hydration-controlled strength. To a certain extent, porosity can be a proxy for geological evolution, and any large near-surface sulfate hydrate deposit on Mars, regardless of formation method, is unlikely to be completely pore free. Therefore, sulfate hydrate deposits on Mars will likely have a strength that is governed by the bulk porosity rather than the strength of the pure solid phase. Terrestrial sulfate hydrate deposits, such as gypsum, have porosities typically in the range of between 1% and 20% [Papadopoulos et al., 1994; Olgaard et al., 1995; Hoxha et al., 2006], and we would expect a similar range to be of most interest for all but the most weakly consolidated martian deposits.

Our samples demonstrated failure mechanisms typical of uniaxial compression tests on terrestrial rocks and ice. Mode I axial fracturing [e.g., Paterson and Wong, 2005] was evident in most samples after failure. Because our sample preparation and experimental method minimized boundary effects at the loading platen-sample interface, axial fracturing is most likely indicative of crack formation and/or opening parallel to the applied stress [e.g., Renshaw and Schulson, 2001; Schulson, 2001; Wachter et al., 2009]. The mechanical properties of our samples can be compared with those of terrestrial salts in uniaxial compression studies, where porosity is explicitly given. In a recent study, the anhydrous salts halite (NaCl) and anhydrite (CaSO₄) were found to have zero-porosity mean UCS values of 18.7 and 23.9 MPa, respectively [Liang et al., 2007], compared with our predicted zero-porosity UCS of the magnesium sulfate system of 35.4 MPa. The relative weakness of the natural salt samples is most likely the result of compositional interbedding between halite and anhydrite [Liang et al., 2007]. The anhydrous sulfates glauberite (Na₂Ca(SO₄)₂) and thenardite (Na₂SO₄) have zero-porosity UCS values of 49 and 20 MPa, respectively, similar to this study [Liang and Zhao, 2004].

The mechanical properties of our samples can also be compared with those estimated for possibly similar deposits on Mars. The most relevant comparative study determined the porosity-strength relationship for light-toned layered deposits near the Mars Exploration Rover Opportunity landing site in Meridiani Planum [Okubo, 2007]. In that study, apparent porosity was measured from Microscopic Imager (MI) observations of rock surfaces ground by the Rock Abrasion Tool (RAT) and related to strength by using the UCS of a terrestrial shale analog, measured in previous experimental studies [Lashkaripour and Dusseault, 1993; Horsund, 2001; Chang et al., 2006]. Figure 7 shows curves for UCS and Young’s modulus as a function of porosity, which are fitted to the combined data of Okubo [2007]. Shale has previously been shown to be a good mechanical analog for martian layered deposits, both through the “grindability” of specific RAT targets in Meridiani Planum [Arvidson et al., 2004] and slope-stability studies in Valles Marineris [Schultz, 2002], and to a certain extent, our study validates this assumption. The porosity-dominated strength properties of our magnesium sulfates are also similar to those determined for a nonwelded tuff from Calico Hills.

Figure 7. Mechanical properties of the magnesium sulfate system as a function of porosity. In each case, the (a) UCS, (b) Young’s modulus, and (c) Poisson’s ratio are plotted as a function of porosity for the experimental results in this study. MS1.25, MS7, and MS11 are represented by diamonds, circles, and squares, respectively, with the fill colors representing the test temperatures. The white lines on the temperature scale represent the test temperatures as given in the scale bar. The white lines on the temperature scale represent the test temperatures of 223, 233, 248, 261, 300, and 323 K. Porosity error bars are the maximum probable error and, in most cases, are smaller than the symbols; vertical error bars are one SD for each experiment. In each case, the best fit relationships described in the text, with one and two SD ranges, are plotted (for the exponential curve in Figure 7c). Also plotted in Figures 7a and 7b are similar best fit curves plotted for the Rover Opportunity RAT data of Okubo [2007] for rocks in Meridiani Planum.
Table 2. Parameter Values for Relationships, Referred to Equations in the Text, Between Porosity and UCS

<table>
<thead>
<tr>
<th>Parameters – Equation (3)</th>
<th>Fit</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$R^2$</td>
</tr>
<tr>
<td>This study</td>
<td>35.55 (4.96) $^{\text{a}}$</td>
</tr>
<tr>
<td>Okubo [2007]</td>
<td>47.77 (4.07) $^{\text{a}}$</td>
</tr>
</tbody>
</table>

$^{\text{a}}$Values in parentheses refer to the standard error in the parameter fit.
$^{\text{b}}$Parameter not varied.

Table 3. Parameter Values for Relationships, Referred to Equations in the Text, Between Porosity and Young’s Modulus

<table>
<thead>
<tr>
<th>Parameters – Equation (4)</th>
<th>Fit</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$R^2$</td>
</tr>
<tr>
<td>This study</td>
<td>6.48 (0.66) $^{\text{a}}$</td>
</tr>
<tr>
<td>Okubo [2007]</td>
<td>23.36 (3.47) $^{\text{a}}$</td>
</tr>
</tbody>
</table>

$^{\text{a}}$Values in parentheses refer to the standard error in the parameter fit.
$^{\text{b}}$Parameter not varied.
5.2. Implications for Magnesium Sulfate Hydrates on Mars

[29] The mechanical properties determined here do not necessarily help determine the conditions under which sulfate hydrates form, but they do help us understand how similar deposits would have behaved since their formation. Any wall slope is only as strong as the weakest layer present, and thus, to a large extent, the stability and possible collapse of walls that contain even relatively thin layers of sulfate hydrates will be governed by the strength of those deposits. In East Candor Chasma, alternating layers of kieserite and polyhydrated sulfates have been observed in CRISM data, with the kieserite beds having steeper slopes than those of the polyhydrated layers [Roach et al., 2008; Murchie et al., 2009]. The relative steepness of the alternating layers is unlikely to be controlled by the original formation method and is more likely representative of the postdepositional evolution of the layers. In this case, the steeper kieserite walls are probably indicative of greater bulk strength than for the polyhydrated layers, which could be due to the porosity effects (the kieserite could be stronger because of a lower porosity than the polyhydrates) and/or inherent differences associated with hydration state (if porosity is homogenous throughout the layers, then there

<table>
<thead>
<tr>
<th>Parameter Values for Relationships, Referred to Equations in the Text, Between Porosity and Poisson’s Ratioa</th>
</tr>
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<tbody>
<tr>
<td><strong>Spherical Pores</strong></td>
</tr>
<tr>
<td>Parameters – Equation (5)</td>
</tr>
<tr>
<td>$n_0$</td>
</tr>
<tr>
<td>This study</td>
</tr>
</tbody>
</table>

aValues in parentheses refer to the standard error in the parameter fit. Parameters in the spherical pore fit are essentially unconstrained.

Figure 8. Example of cyclic stressing results with an MS7 sample (run 8) loaded and unloaded at a strain rate of $1.7 \times 10^{-6}$ s$^{-1}$ at 300 K. (a) Loading path showing the increasing stress amplitude procedure, with each loading and unloading portion of a cycle indicated. The sample failed during the ninth cycle. (b) Stress as a function of radial and axial strain, showing significant dilatancy.

Figure 9. Evolution of elastic moduli with increasing cycling stressing. (a) Mean Young’s modulus of the quasielastic loading portion for both MS7 runs 7 (triangles) and 8 (circles) as a function of cycle number. (b) Mean Poisson’s ratio of the quasielastic loading portion for MS7 run 8. Error bars in this case are smaller than the data points. In each case, experimental conditions are given in addition to nominal fits to experimental data.
in this study plotted as a function of the depth-porosity relationships given by Clifford [1993]. In this figure, we use the porosity-relationships for UCS, Young’s modulus, and Poisson’s ratio given by equations (3), (4), and (6), respectively. We consider the two cases of Clifford [1993], with surface porosities of 20% and 50%, with porosity increasing with depth according to an exponential relationship. It is evident that, with all other factors being equal, the UCS and Young’s modulus of magnesium sulfate hydrates, both increase with depth, as a result of the reduced porosity, whereas Poisson’s ratio decreases. Surface porosities of close to 50% have been observed for the RAT grind target Virginia, with the resultant predicted UCS and Young’s modulus of this rock being 3.55 MPa and 0.42 GPa, respectively [Okubo, 2007]. Our predicted surface values of UCS and Young’s modulus at 50% porosity are more than double those predicted for Virginia, indicating that the shale analog might not be appropriate at these high porosities and/or that local factors such as preferred orientation or grain size might play a role in weakening the sulfate-rich rocks at Meridiani Planum. Thus, at the surface, our results probably best represent maximum values of mechanical properties of sulfate hydrates, which could be applied to gypsum dunes observed in the North Polar region [Langevin et al., 2005]. However, the most extensive deposits of magnesium sulfate hydrates have been observed by orbiting infrared spectrometers to occur at near-equatorial latitudes. Observations by the OMEGA instrument onboard the Mars Express spacecraft show the global distribution of hydrated minerals on Mars and indicate large-scale concentrations of hydrated deposits in Valles Marineris and chaos regions [e.g., Bibring et al., 2006]. The OMEGA observations serve as an effective context for higher spatial resolution, multispectral images obtained by the CRISM instrument onboard Mars Reconnaissance Orbiter. Recent CRISM observations have identified outcrops of polyhydrated sulfate-rich layers in Aram Chaos, occurring in a 500 m thick deposit, which are overlain by approximately 500 m of an erosion-resistant cap unit [Lichtenberg et al., 2008]. This band of sulfate hydrate deposit is plotted as a function of depth in Figure 10 to illustrate how our results can be of use to future studies concerned with the strength and stability of similar deposits on Mars. For example, at depths similar to those observed at Aram Chaos, any layers dominated by sulfate hydrates could have strength properties significantly higher than expected for similar deposits at the surface. Thick hydrate layers have also been predicted to occur at greater depths on Mars. Kargel et al. [2007] invoke thermally insulating salt and gas hydrate lenses 1 km thick, with upper surfaces at depths of up to 2 km, as being responsible for hydrologic processes such as chaos or gully formation. The mechanical behavior and ultimate collapse involved in such a process will be at least partially governed by the mechanical properties of the hydrates involved, in addition to other factors such as compositionally induced freezing point depressions and the local geothermal regime [Kargel et al., 2007]. Our results are important in such studies, although further experiments are required to investigate the effect of confining pressure on the mechanical properties of sulfate hydrates.

[30] The porosity of sulfate-rich deposits at the martian surface has been estimated from Opportunity RAT data [Okubo, 2007], but it can also be predicted as a function of depth using theoretical depth-porosity relationships. Figure 10 shows the mechanical properties determined in further experiments on different hydrates of similar porosities, or of one or more hydrates with a range of porosities, are required to address this uncertainty.
strain rates under uniaxial conditions, could be indicative of the propensity of these hydrates to undergo time-dependent deformation [Durham et al., 2005] or pressure-induced melting [Hogenboom et al., 1995]. The ductile deformation of anhydrous and hydrous salts is an important process on the Earth, forming diapiric intrusions and hydrocarbon traps, and there is evidence for similar deformation mechanisms operating on Mars at both local and regional scales despite the lower temperatures. HiRISE imagery reveals fold and thrust fault structures, on the order of hundreds of meters to kilometers, in interior layered deposits in SW Candor Chasma [Okubo et al., 2008; Okubo, 2010], indicative of combined ductile and brittle processes, respectively. Our observation of ductile behavior in meridianite at low temperatures under uniaxial load suggests that similar deposits on Mars could deform in a ductile manner under present-day surface conditions. Ductile creep could occur in sulfate hydrates at lower strain rates than considered in this study if the confining pressure was increased [Durham et al., 2005]. The ductile behavior of salts has also been implicated in regional-scale gravity spreading in the Thaumasia Plateau region of Mars [Montgomery et al., 2009]. The elevated pressure and temperature at the depths required for this gravity spreading model will increase the likelihood of ductile deformation in magnesium sulfate hydrates, and hydrates in general, even at low strain rates, because our results show that ductile creep can begin at driving stresses as low as ~15 MPa (Figure 5).

[32] Our cyclic stressing tests can be related qualitatively to periods of changing obliquity on Mars through responses both external and internal to deposits of sulfate hydrates. Cyclic stressing of sulfate hydrate layers could occur on Mars owing to the response of the atmosphere to obliquity-related insolation changes [e.g., Laskar et al., 2002, 2004]. Atmospheric deposition of dust and/or ice at low latitudes during periods of high obliquity could increase the load on preexisting layers; for example, an average deposition rate of 0.05 cm yr\(^{-1}\) [Laskar et al., 2002] during 10 Ma yields an overlying deposit 5 km thick, giving rise to a confining load of ~30 MPa. Obviously, during periods of low obliquity, aeolian erosion and sublimation of ice will remove some of the deposited material, hence reducing the load. Similar periods of cyclic loading could also occur through periodic burial of sulfate hydrate deposits by lava flows or impact ejecta, although regularly cyclic bedding observed at the poles [Laskar et al., 2002] and low latitudes [Lewis et al., 2008] appears to rule out such stochastic processes for these deposits. The intrinsic properties of sulfate hydrate deposits, such as thermal expansivity, conductivity, and gas diffusivity, would also respond to obliquity-related temperature and humidity changes regardless of deposition loading. Our results suggest that, although cyclic loading might not immediately change the overall strength of sulfate hydrate layers on Mars, this cyclicity will affect the porosity, and hence the long-term strength and water-storing capacity of these deposits.

6. Conclusions

[33] We have carried out uniaxial compression experiments on stable phases in the magnesium sulfate-water system to determine the mechanical properties of similar deposits on Mars. In this study, we attempted to measure UCS, Young’s modulus, and Poisson’s ratio. Our synthetic samples of kieserite (MS1.25), epsomite (MS7), and meridianite (MS11) have mean porosity values of 47.6%, 11.4%, and 2.9%, respectively, and mean UCS values of 6.3 ± 0.7, 12.9 ± 1.8, and 30.1 ± 4.5 MPa, respectively. As a system, magnesium sulfate hydrates seem to have strengths that are controlled predominantly by the sample porosity, showing a negative trend with UCS. Young’s modulus also shows a similar relationship with porosity, with MS1.25, MS7, and MS11 having mean Young’s modulus values of 0.8 ± 0.1, 2.9 ± 0.4, and 5.9 ± 0.8 GPa, respectively. We successfully measured Poisson’s ratio in only 20% of our tests, resulting in errors sufficiently large to preclude determination of a relationship with porosity with any confidence. Porosity was measured using relative density analysis and, in representative samples, verified with other methods including fluid saturation and gas displacement.

[34] Although our tests were unable to quantify any systematic relationship between hydration state and mechanical properties, the different porosities produced by consistent sample preparation methods suggest that the addition of non-cation-coordinated water molecules likely reduces the bulk strength of sulfate hydrates. We expect that the mechanical properties of sulfate hydrate deposits on Mars will be dominated by the bulk porosity rather than by the strength of the pure solid phase. Further experimental work is required to produce different hydrate phases of similar porosities, or vice versa, to identify any possible hydration-related strength relationship for application to alternating layers of sulfate hydrates as wall rock on Mars. Future experiments should also address the possibility of pressure-induced incongruous melting, which could lead to ductile behavior, at temperatures below those expected at the respective melting temperatures of the different hydrate phases.

[35] To simulate possible obliquity-related depositional and erosional periods on Mars, we also carried out some cyclic stressing tests. The three samples used in the cyclic tests showed similar bulk mechanical properties to those in the single loading tests, although a gradual compaction and reduction in sample porosity, rather than just an increase in crack damage, was observed with each loading cycle. Applying these preliminary cyclic results to similar deposits on Mars suggests that any obliquity-related evolution of mechanical properties will depend on local factors such as bulk density, porosity, and, hence, formation mechanism, in addition to the overall stress history.

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