Impact-induced water loss from serpentine, nontronite and kernite

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Abstract—Preliminary experiments have been conducted to study shock-release of volatiles from minerals. Impact-induced loss of bound water from hydrous minerals has been observed, using infrared absorption and X-ray powder diffraction techniques. Serpentine (Mg$_3$Si$_2$O$_7$(OH)$_6$) and nontronite (5.3Ca$_2$Fe$_2$Si$_3$O$_{10}$(OH)$_2$·8H$_2$O) were shocked and recovered from pressures of up to 18 GPa, using one-dimensional shock-inertion techniques. Kernite (Na$_4$Mg$_8$Si$_8$O$_{22}$·4H$_2$O) was impacted by a spherical pyrex projectile traveling at 4.89 km sec$^{-1}$, which produced a peak pressure of ~33 GPa. The infrared absorption spectra indicate that some of the bound water from these three minerals was released as a result of shock compression and subsequent rarefaction. This evidence is supported by the recovery of small amounts of vapor from the serpentine shocked to 21.5 GPa and the nontronite shocked to 18 GPa. The recovered vapor is inferred to be water from the shocked minerals. X-ray diffraction spectra indicate no major changes in the unit cell dimensions of the two silicates, except for a decrease in the lattice constant in the c-direction of the nontronite, consistent with the loss of interlayer water.

INTRODUCTION

Central to any model of the formation of the terrestrial planets is the degassing history. Extensive evidence supports the hypothesis of Fanale (1971) that the loss of volatiles from the solid earth was early and rapid. Arthursen et al. (1974) and Benlow and Meadows (1977) demonstrated that a primitive atmosphere will form as a result of strong shock compression and heating associated with the accretion of large planetesimals. Süss (1979), Jakosky and Ahrens (1979), and others have used such an atmosphere as a starting point for recent models of atmospheric evolution. The concept of an impact-created early atmosphere is not inconsistent with the idea of a later slow migration of volatiles from the mantle to the surface (Walker, 1977). In fact, energy derived from accretional impacts may have mobilized volatiles into energetically favorable states for later removal from the solid mantle. Lange and Ahrens (1979) and Lange (1980) have calculated the shock pressure necessary to release water from the hydrous minerals brucite and serpentine with varying initial porosity. These calculations were based on the entropy-gain method of Ahrens and O'Keefe (1972) and made use of thermodynamic and shock wave data for brucite and serpentine. The Gruneisen parameters used in the
entropy calculations had to be estimated because they have not been determined experimentally for these minerals. Thus the calculated pressures required for vapor release are dependents on the Grometise parameters used and are subject to the uncertainties in them. These uncertainties are difficult, if not impossible, to estimate without determining the Grometise parameters experimentally.

We chose a more direct method of determining the efficiency of impact-induced devolatilization of hydrous minerals, which bypasses theoretical calculations altogether. Our approach was to carry out exploratory shock-vaporization experiments which allowed shock-induced volatile release to be observed in the laboratory. The information obtained should help to constrain theories of atmospheric formation and evolution.

EXPERIMENTAL TECHNIQUES AND SAMPLE PREPARATION

Six successful shock-recovery experiments were conducted on three hydrous minerals. The critical data are summarized in Table 1. Three experiments were performed on serpentine (Mg₂Si₄O₁₀(OH)₆) and two on nontronite (0.5 Ca₆Fe₄₋₅(Si₄Al₂Si₂O₁₀(OH)₂)₆H₂O) using methods similar to those described by Gibbons et al. (1979). In each of these experiments the target was shock-loaded by a flat-faced metal projectile accelerated to high velocity by a propellant gun. Three of the experiments—two serpentine and one nontronite—were carried out on sample disks sandwiched between two polished metal plates and pressed into metal target cylinders in an arrangement similar to that described in detail by Gibbons (1974). A 30-mm calibre gun was used to launch the projectiles in these three experiments.

One serpentine and one nontronite experiment employed a modified target assembly designed to isolate the solid sample and to capture any vapor liberated (Fig. 2). The presence of captured vapor is sufficient to show that volatile release has occurred. When vapor escapes from the sample it expands into an evacuated chamber and can be condensed through a valve into a glass ampoule and weighed.

A 29-mm calibre gun was used to accelerate the projectile in the serpentine experiment, and a 40-mm calibre gun was used in the nontronite experiment.

In all the serpentine and nontronite experiments, the flyer plates and target cylinders were stainless steel 304 (6% Fe, 21% Cr, 9% Ni). Peak shock pressures in all cases were determined by applying graphical impedance matching techniques to the Hugoniot data for the flyer plate and target material (McQueen et al., 1970).

One impact experiment was carried out on a kersite (Na₂Ca₂Si₅O₁₂·4H₂O) crystal. The projectile, a 3.18-mm diameter pyrex sphere, was fired from a light gas gun into the single crystal block of kerinite (approximately 15 cm on edge). This configuration produces a two-dimensional, axially symmetric impact much like a cratering experiment. Since the kerinite crystal was much larger than the projectile, the shock wave generated was similar to a natural event. The ejecta fragments from the impact were captured by an aluminum witness plate and
<table>
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<th>Shot #</th>
<th>20-54a**</th>
<th>20-551*</th>
<th>20-552*</th>
<th>40-49**</th>
<th>20-550*</th>
<th>AVG-706900***</th>
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<td>77.8 GPa</td>
<td>18.1 GPa</td>
<td>30.0 GPa</td>
<td>28-38 GPa</td>
</tr>
</tbody>
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* Performed at Catter, 20 ton gun
** Performed at Calle-b, 40 mm gun
*** Performed at Ames Vertical Gun Range
† Performed in target model to capture vapor.
recovered for analysis. Because no Hugoniot data for kermite exist, an exact calculation of the peak pressure induced could not be made. To estimate the peak pressure we used the measured Hugoniots of gypsum, which is similar in density and hardness to kermite, and applied the graphical impedance matching method.

The principal mineral chosen for study was serpentine, which is believed to have been one of the most abundant hydrous silicates present in the accreting planetesimals because it is a major hydrous constituent of carbonaceous chondrites (Kaula, 1968). Serpentine contains 15% H_2O by weight. Lange (1980) estimated that serpentine, with an initial porosity of less than 10%, loses water at shock pressures between 40 and 60 GPa.

The source of the serpentine was Warren County, New York. Electron microprobe data showed the composition of the samples to be homogeneous and close to the magnesium-rich end member. The serpentine is mainly composed of the polymorph antigorite, as determined by X-ray diffraction and infrared absorption. The mean measured density of the specimen to be shocked was 2.53 g cm^{-3}, because the single crystal density of antigorite is 2.6 g cm^{-3} (Deer et al., 1966). We conclude that the upper bound for the porosity of our samples is 5%. Some of the density difference is probably due to impurities—the actual pore space is considered to be very small.

The surfaces of the serpentine sample disks were polished to provide good contact with the steel driver plates. Samples for all three serpentine experiments were dried in an evacuated oven at 100°C for 24 hours; they were shocked, to remove as much unbound and adsorbed H_2O as possible.

The second mineral we studied was a smectite, contractite. Due to its chemistry (Haid et al., 1976; Toulmin, 1977) and overall spectral characteristics (Singer et al., 1979; Weldon et al., 1986), montomorillonite is believed to be a good candidate for the major constituent of the Martian fines. The montomorillonite was collected in Riverside, California and was the same material investigated by the Viking Inorganic Chemistry Team. The sample was a fine powder and was pressed into the steel target cylinders to a density of about 2.7 g cm^{-3}. The montomorillonite sample was not subjected to a heat treatment, so interlayer and adsorbed water was not removed before the samples were shocked.

We chose to use kermite in the two-dimensional impact experiment because it is a hydrous mineral that could be obtained in a sufficiently large homogeneous block. An appropriately-sized single crystal of kermite was collected from the U.S. Borax Mine near Bakersfield, California. The crystal was encased in concrete with a smooth face exposed. No heat treatment was conducted prior to the experiment.

ANALYSIS AND RESULTS

The solid material recovered from the shock experiments was analysed using infrared absorption. Particular attention was paid to the absorption bands known to be associated with the vibration of molecular water and hydroxyl ions. X-ray diffraction of the shocked minerals was also employed, so that structural changes could be characterized.
Fig. 1. Schematic diagram of target assembly designed to capture vapor released from minerals shocked to high pressure. (A) Before impact. Flyer plate approaches from left at high velocity. Sample disk is in place in cylindrical well with small plates pressed into the well behind it to provide a high impedance rear surface. (B) At impact. Shock wave propagates into steel cylinder, overburdening the sample disk up to the Hugoniot pressure of steel. (C) After impact. Shock is relaxed to low pressure, and any vapor liberated fills the expansion chamber. Small plates and shocked sample material are carried into the expansion chamber by momentum gained from the shock wave.
Fig. 2. The infrared absorption spectrum of an unheated sample of serpentine is shown, along with the spectra for material recovered from two different shock experiments. The resonance at 3600 cm⁻¹ is due for the OH⁻ stretching mode. There are two broad peaks for free water: the water-water hydrogen bond mode at 3400 cm⁻¹ and the HO₂ bending mode at about 1630 cm⁻¹. The large peaks at the low wavenumber end of the spectra are associated with the Si-O bond. Note that the relative peak height of the OH⁻ stretching resonance decreases with increasing shock pressure, indicating a loss of structural water. The small peak near 2900 cm⁻¹ is due to CF₄ in the sample chamber.
Samples to be used for infrared analysis were ground into a fine powder. The powdered samples were mixed with KBr, reground, and pressed into pellets. In each case, 1 mg of sample was used with 180 mg of KBr. Care was taken to standardize the sample preparation.

Infrared spectra for material recovered from shots 20–551 (serpentine, 50 GPa), and 20–552 (serpentine, 28 GPa) are shown in Fig. 2, with the spectrum of unshocked serpentine. Because the spectrum of the material recovered from shot 20–544 (serpentine, 21 GPa) was identical to the spectrum for unshocked serpentine, it was not included. Shocked samples show a decrease in the intensity of the absorption peak at 3800 cm\(^{-1}\) relative to the K-O stretching and bending peaks at the low-wavenumber end of the spectrum. The decrease is more marked for the serpentine shocked to the higher pressure. There is also a broadening of absorption peaks, which is indicative of non-uniform local potentials. This could be brought about by increased internal disorder. The broad peaks at 3400 cm\(^{-1}\) and 1620 cm\(^{-1}\) are due to absorption by molecular water (Farmer, 1974), and do not seem to be dependent on whether the sample was shocked. This suggests that they are due to water adsorbed on the surface of the material, the amount of which is subject to change during post-experiment sample treatment, such as the length of time the shocked material was left in the target cylinder before it was recovered. When infrared spectra were measured after vacuum heating the sample pellets at 100°C, the broad molecular water peaks were all diminished; however, the other absorption peaks were unaffected. Upon further investigation we found that the only peaks sensitive to sample preparation and handling were the molecular water absorptions at 3400 and 1620 cm\(^{-1}\).

X-ray powder diffraction spectra for the shocked and unshocked serpentine were obtained using a General Electric model 700 diffractometer with a copper source, operated at a voltage of 45 kV and a current of 17 mA. Portions of these spectra corresponding to the 7.25 interlayer lattice constant are shown in Fig. 3. Any structural changes due to shock loading the serpentine do not appear to be within the resolution of this instrument.

The infrared spectra of montmorillonite have the qualitative characteristics of serpentine (Fig. 4). The free water peak at 3400 cm\(^{-1}\), however, includes a contribution from interlayer water, so changes may be more significant in this case. Both this peak and the OH\(^{-}\)-peak, which corresponds to structural water, show marked decreases in the specimen from shot 20–550 (30 GPa). Heating the montmorillonite KBr pellets decreased the 3400 cm\(^{-1}\) peaks to about the same low level, which was only slightly below that peak of unshocked shocked montmorillonite. As for the serpentine, the OH\(^{-}\)-peaks were unaffected by heat treatment.

According to X-ray powder diffraction data for the montmorillonite from shot 20–550, the shock-loading caused a significant collapse of the basal layer. The other d-spacings were relatively unchanged, suggesting that the unit cell parameters in the silicate sheets were merely undisturbed and the major shock-induced structural change in the montmorillonite was the decrease in the distance between the layers.

The infrared spectrum of ejecta fragments recovered from the kermitite shot (AVG-79909), along with the spectrum of unshocked kermitite, is shown in Fig.
5. The recovered fragments were imbedded in the aluminum witness plate above the impact site, and probably came from the near field of impact where material was most heavily shocked. The krotite spectra look similar to the nontronite spectra in the region of the OH⁻ and H₂O absorption peaks near 3400 cm⁻¹. The peak due to OH⁻ stretching at 3550 cm⁻¹ does not show as marked a decrease for the shocked krotite as for the shocked nontronite. The free water peak of the krotite spectrum was broadened somewhat.

Volatile release has been corroborated by direct measurement in shots 20–544 and 40–492. In 20–544, 2.62 mg of gas was recovered, amounting to 0.66% of the sample weight. Serpentine contains 15% H₂O by weight, so 4.4% of the available water in the sample was released, assuming this is the only source of the vapor recovered. Similar measurements were made for nontronite from 40–492, showing a recovery of 9.17 mg of gas, amounting to 3.06% of the sample weight.

DISCUSSION

The differences in the infrared spectra of shocked and unshocked serpentine can be explained by the loss of structural water. Greater water loss would be expected
for higher shock pressures. Our data support this over a limited pressure range (Fig. 2). The loss of hydroxyl is accompanied by a small amount of structural modification of the silicate sheets. This is manifested in the broadening and overall shape-change of the peaks associated with the Si-O bond (those below 1200 cm⁻¹).

Even though released vapor was directly detected, the infrared spectrum of material recovered from shot 20-544 showed no evidence of water loss. This apparent inconsistency can be explained by the fact that the sample was too large. The extralarge sample was used in this experiment to increase the total volume of vapor released so it could easily be detected in our gas collector. The sample was so large, however, that only about 50% of its total mass was shocked to the peak pressure of 25.5 GPa. In most of the sample, the shock wave was attenuated by dilation waves from the sides of the target cylinder, so the material never reached the calculated peak pressure. Because the violent motions associated with the subsequent rarefaction effectively pulverized and homogenized the solid material, it was impossible to recover only the highly shocked portion for infrared analysis. It is unlikely that the vapor detected in shot 20-544 was adsorbed water because that had already been removed by heating of the sample just prior to the shot.

**Fig. 4.** Detail of the OH stretching resonance at 3350 cm⁻¹ and the H₂O hydrogen bond resonance at 3400 cm⁻¹ in the infrared spectra of unshocked montmorillonite and montmorillonite shocked to 20 GPa. Note that both peaks are smaller for the shocked material.
In all three shock wave experiments on serpentine we detected the release of water either directly or by obtaining infrared spectra of the recovered solid. The peak pressures achieved in these experiments were well below the 60 GPa estimated by Lange (1980) to be necessary for incipient vaporization of water from serpentine. In his calculations the shock heating was assumed to be uniform behind the shock front. If, however, the dissipation of energy in the shock wave is heterogeneous, there will be small regions of shocked material where the temperature and internal energy is much greater than average (Grady, 1977). The specific entropy in these localized regions might then surpass that required to release water upon rarefaction, even though the average specific entropy behind the shock front is below this value.

Shock loading also caused a major loss of structural water from the nontourite as indicated by the reduction in the OH peak height in the spectrum of sample 20-550 (Fig. 4). The shock should also have driven off much of the less tightly bound interlayer water. Because the interlayer water is easier to remove, a decrease in the molecular water peak relative to the OH peak might be expected. However, in shot 20-550 it appears that most of the hydroxyl water was lost. This can be explained if we consider that after the impact the shocked material is in intimate contact with the released water vapor. Some of the released water will be reabsorbed as the system begins to return to equilibrium. At post-shock temperatures, water is prevented from returning to the structural positions by energetic obstacles to diffusion processes. However, water is readily diffused and reabsorbed between the layers in nontourite. Collapse of the basal layer of the monticellite from 14.9 to 11.7 Å, shown by the X-ray diffraction data, suggests
that a loss of about 2/3 of the interlayer water occurred upon impact. X-ray and infrared data indicate that both interlayer and structural water were released. It appears that some vapor was reabsorbed as interlayer water but not enough to return the interlayer water to the original quantity. The vapor recovered from 0-492 is a significant fraction of the total mass of the sample. Most of this vapor probably came from interlayer and adsorbed water, as the montmorillonite was not desiccated by a heat treatment before it was shocked.

It is important to remember that the serpentine and montmorillonite samples were not brought to their peak pressure in the same way they would be for an impact in nature. In reality, material would be loaded to high pressure by a single shock wave produced by the impact of two bodies. In these experiments, mineral samples were never impacted to high pressure by consecutive reflected shock waves over a finite time interval (Neale, 1980). Material loaded by this process remains closer to the isentrope than material loaded to the same pressure by a single shock. Thus multiply-shocked material does not generally reach as high a temperature or specific entropy as naturally shocked material and will tend to retain a greater percentage of its volatiles. For this reason we believe our experiments provide a minimum estimate of shock-induced volatile release.

Another difference between experimental and natural shock-loading is the sample container. In nature the shocked mineral would not be surrounded by stainless steel. Thus we should also consider the post-shock temperature of the stainless steel container and its effect on the amount of volatilization. Post-shock temperatures of stainless steel have been measured for shock pressures in the range considered here (Raikes and Abrets, 1979). The post-shock temperatures corresponding to shock pressures of 16.0, 23.0, and 43.0 GPa, were measured to be 145, 195, and 320°C, respectively. Experimental work in the kinetics of dehydration of serpentine (Brindley and Hayomi, 1963) have shown that the effects of these temperatures on serpentine for the times required for the target to cool (~10 minutes) are very small. In shots 26-544 and 40-492, most of the shocked sample did not remain in contact with the hot steel; immediately after the shot, the sample was scattered into the expansion chamber along with the splash plates (Fig. 1). In the monmorillonite shots a color change accompanied the release of volatiles (Weldon et al., 1985). The part of the sample that remained in the more intimate contact with the shock-heated portion of the stainless steel container showed no more color change than the portion that exploded into the expansion chamber. This suggests that the heating of the sample by the stainless steel was not significant.

Comparison of the infrared spectra of the shocked and unshocked kerinite (Fig. 5) reveals differences similar to those between the two mica montmorillonite spectra in Fig. 4. The intensity of the OH-stretching vibration diminished slightly, relative to the molecular H2O vibration in the shocked sample. The molecular H2O absorption peak broadened and changed shape, indicating a change in the local environment of the unbound water. A reasonable interpretation is that part of both the structural and nonstructural water was released by the impact and later reabsorbed by the shocked kerinite.

Because of the nature of the experiment, it is impossible to give an accurate
account of the shock history of the keratite ejecta fragments we studied. Material from the new field of an impact is ejected at very high velocity, often higher than the projectile velocity (Gault et al., 1962). If the keratite ejecta we recovered came from near the point of impact it was effectively shocked twice—once during the primary impact and once when it imbedded in the aluminum witness plate. Some of the ejecta fragments, however, may have originated at points away from the impact. The important result of the keratite experiment is that it gives some evidence that water was rearranged in a hydrous mineral by a shock experiment that closely models a natural impact.

CONCLUSION

Five experiments presented here show strong evidence of shock-induced water loss from hydrous silicates. Released water was recovered in the two lowest pressure experiments, which were designed to capture vapor. The target design in the three higher pressure experiments did not allow collection of released vapor; however, infrared and X-ray spectra of the recovered solids indicate that water was indeed released. The quantity of water released increases with shock pressure over the range studied. These data also contain information on the type of water (hydroxyl or molecular) that was released from the silicates by shock-loading.

The minimum shock pressure required for incipient vaporization of water from serpentine is less than 23.5 GPa, which is well below the 60 GPa estimated by Lange (1988). While more detailed and extensive experimentation must be carried out before more quantitative results can be obtained, we believe the difference is significant. Interlayer water is lost from montmorillonite at pressures as low as 18 GPa, and a significant quantity of water is lost from the structure at 30 GPa.

We have observed that structural, interlayer and absorbed water in hydrous minerals can be released by shock pressures generated by two types of impacts, one which resembles the type which would occur in nature, a fact which has important consequences regarding the formation of planetary hydrospheres and atmospheres. We believe that impacts played a major role in the release of volatiles from materials in the proto-planetary objects during their accretional stages. There is a net mobilization of water in hydrous minerals by impact release and subsequent redissolution into less tightly bound configurations. In this way water can be made more available for reactions and more easily mobilized for later episodes of volatilization by accretional and endogenic processes.

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