Dehydration Kinetics of Shocked Serpentine

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Experimental rates of dehydration of shocked and unshocked serpentine were determined using a differential scanning calorimetric technique. Dehydration rates in shocked serpentine are enhanced by orders of magnitude over corresponding rates in unshocked material, even though the impact experiments were carried out under conditions that inhibited direct impact-induced devolatilization. Extrapolation to temperatures of the Martian surface predicts that dehydration of shocked material would occur 20 to 30 times more rapidly than for unshocked serpentine. The results indicate that impact-induced reactions and associated atmospheres would reach chemical equilibrium much more quickly than calculations based on unshocked material would indicate, even during the earliest, coldest stages of accretion. Furthermore, it is suggested that chemical weathering of shocked planetary surfaces by solid-powder reactions would be sufficiently rapid that carbonaceous micro-fossils should form.

INTRODUCTION

Impact into volatile-bearing rocks and minerals may have strongly influenced planetary accretion and the development of primitive planetary atmospheres. A number of accretion models have been proposed that focus on the importance of the extent of impact-induced devolatilization as a function of impact velocity (or planetary size) in determining the course of planetary atmospheric and thermal evolution (Arakawa et al., 1974; Benoune and Mathews, 1977; Jakobson and Ahrens, 1979; Lange and Ahrens, 1982a; Ahrens and Matzen, 1985). Impact-induced devolatilization of minerals was first observed by Boshgagh et al. (1980) in hydrous silicates. Subsequent studies have extended the observations to hydrous minerals in higher shock pressures (Langme et al., 1985) and have investigated shock devolatilization in carbonates (Doshag et al., 1982; Lange and Ahrens, 1985) and meteorites (Doshi et al., 1986).

Experimental

The impact experiments were performed on a nearly pure magnesium end member polycrystalline felsitic serpentine [Na2Si2O5(OH)4] collected near Glade, Arizona (Caltech Mineral Collection, Specimen Number 321). The bulk chemical analysis is shown in Table 1. The density of the mineral is 2.95 ± 0.02 g/cm³. Solid recovery: impact-induced devolatilization experiments were performed on the silicon powder gun at the California Institute of Technology using the stainless steel aerogel chamber assembly sketched in Fig. 1. Using this assembly, sample masses on the order of 0.5 to 1 g could be impacted and recovered. The sample was inserted into the assembly as a powder, and then pressed in by the containing plug. Sample densities were calculated from the mass of mineral added and the final volume of the sample. Densities of approximately 8% of the bulk mineral density were attained. Sample dimensions were about 1.0 cm in diameter by 0.5 cm thick. The impacted surface-to-sample distance was approximately 0.5 cm. An attempt was
made to provide venting by scoring the sides of the containing plug behind the sample and by providing an escape tube out the back of the assembly. The results indicate that this attempt was not entirely successful and the data from this study (shown in Fig. 2) are indicated as partially vented. For impact velocities up to 1.25 km/s (shots 692 and 693, $P_{\text{peak}} = 25.0$ and 27.5 GPa, respectively) there was no impact-induced devolatilization, while an impact velocity of 1.55 km/s (shot 694, $P_{\text{peak}} = 35.4$ GPa) resulted in 10% devolatilization. Previous results (Lange et al., 1985; Tyburczy et al., 1986) indicate that 10% to 40% devolatilization would be expected had the chamber been adequately vented (Fig. 2). Lange et al. (1985) and Tyburczy and Ahrens (1985, 1986) discuss the problems of vented versus unvented sample assemblies in impact-induced devolatilization experiments.

Shock pressures were calculated using a one-dimensional implosion match calculation (Jetter et al., 1980). We report both the initial shock pressure and the peak reverberated shock pressure in Table 2. Problems with nonlinear propagation of shock waves and design of recovery thrusters are discussed by Graham and Webb (1984). Equations-of-state parameters for stainless steel were taken from Murad (1980), for serpentine we used initial (nonporous) density $\rho_n = 2.50$ g/cm$^3$, $C_p = 5.30$ km/s, and $\gamma = 0.78$ (Tyburczy and Ahrens, in preparation), where shock velocity $U_s$ and particle velocity $u_p$ are related by $U_s = C_p + u_p$. The Hugoniot of porous serpentine was calculated using the relation:

$$P_{\text{sh}} = P_{\text{Hug}} \left[1 - \frac{\gamma}{\gamma_{\text{Hug}}}(\rho/\rho_{\text{Hug}}) - 1/2\right] / \left[1 - \frac{\gamma}{\gamma_{\text{Hug}}}(\rho/\rho_{\text{Hug}}) - 1/2\right] \left(1 \right)$$

(ABracks and O'Keefe, 1972). In equation (1) $P_{\text{Hug}}$ is the Hugoniot pressure of the porous material, $P_{\text{sh}}$ is the Hugoniot pressure at $\rho_{\text{Hug}}$ of the nonporous material, $\gamma$ is the Gruneisen parameter, $\rho_n$ is the Hugoniot density, $\rho$ is the initial density of the nonporous material, and $\rho_{\text{Hug}}$ is the initial porous material density. The Gruneisen parameter is calculated using $\gamma = \gamma_{\text{Hug}}$ ($\rho/\rho_{\text{Hug}}$)$^\gamma$ with $\gamma_0 = 1.0$ and $n = 1.0$ (Tyburczy and Ahrens, in preparation). Initial densities, impact velocities, and calculated initial and peak shock pressures are listed in Table 2. Experimentally determined errors in $\rho$, $P_{\text{sh}}$, and projectile

### Table 2. Experimental results

| Shot Number | Initial Density $\rho$ (g/cm$^3$) | Projectile Velocity $V$ (km/s) | Initial Shock Pressure $P_0$ (GPa) | Peak Shock Pressure $P_{\text{sh}}$ (GPa) | DSC Heating Rate $K$ (W/m$^2$ K) | Tram of Water Loss $W_{\text{water}}$ (Kg) | Activation Energy $E_a$ (KJ/mole) | log (Av) (sec$^{-1}$) | Impact-Induced Devolatilization (%) |
|-------------|----------------|----------------|----------------|----------------|------------------|----------------|----------------|----------------|----------------|----------------|
| Unhocked    | -              | -              | -              | -              | 25               | 722             | 10             | 692            | 5              | 340             | 16.1            | 0              | 0.2 |
| 692         | ±0.04          | ±0.02          | ±0.8           | ±0.2           | 10               | 641             | 5              | 641            | 2              | 220             | 10.3            | 0              | 0.0 |
| 693         | ±0.04          | ±0.02          | ±2.0           | ±0.2           | 25               | 669             | 2              | 598            | 2              | 10               | 0.6             | 1              | 0.0 |
| 694         | ±0.04          | ±0.03          | ±2.4           | ±0.4           | 25               | 675             | 10             | 643            | 5              | 220             | 10.2            | 1              | 16.0 |

Fig. 1. Schematic diagram of the large-volume, solid recovery sample chamber assembly. Sample cup and plug, 304 stainless steel. Split plunges and ring, cold-rolled steel.
velocity $V_S$ were assumed to be independent and were propagated through the impedance match relations and equation (1) to yield waterivities in initial and peak shock pressures (Breitinger, 1969). Estimates of peak and postshock temperature, calculated using the serpentine equation of state parameters (Tybercy and Aloian, in preparation) and incorporating the effects of sample porosity, are $T_{\text{peak}} = 640$, 680, and 920 K and $T_{\text{postshock}} = 510, 530, \text{and} 680$ K for shots 692, 693, and 694, respectively.

Powder X-ray diffraction analyses of the shocked serpentine are consistent with previous results for shocked serpentine (Boskougl, 1968). The shocked material shows a reduction in intensity of the serpentine peaks and an increase in background level, but there is no variation in the position of the peaks that is, there is no variation in the lattice parameters of the shocked material.

Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) of shocked and unshocked samples were performed over the temperature range 300° to 1100°C using a Mettler Thermobalance 2000C. Sample size was approximately 20 mg. Analysis was performed in a nitrogen atmosphere. The extent of impact-induced devolatilization was determined by comparison of TGA analyses of shocked and unshocked material. Figure 5 shows the DSC curves obtained using heating rates of 2, 5, 10, and 25 K/min for the shocked and unshocked materials. In each analysis, the endothermic (downward) peak occurring at temperatures between about 600°C and 700°C is the water-loss peak. The results indicate that for equal heating rates, there is a 50°C to 70°C reduction in the temperature of the water-loss peak for the shocked material relative to the unshocked material, consistent with the more qualitative results of Lange et al. (1985) and Lange and Abaren (1986). Furthermore, there is a systematic increase in the temperature and width of the water loss peak with increasing heating rate.
where $\phi$ is the experimental heating rate. The maximum rate of decomposition occurs at the temperature of the maximum in the DSC curve $T_m$. By setting $d(\phi)/dt$ (d$A_2$/dt) to zero and rearranging one obtains

$$\ln \left( \frac{\phi}{T_m} \right)^2 = -E_a/RT_m + \ln \left( \frac{A_2}{RT_m} \right)$$

(5)

This variation indicates that previous attempts to derive kinetic and thermodynamic information on shocked materials from TGA curves without consideration of the experimental heating rate affects give only qualitative results (Lange and Ahrens, 1982b, 1983; Lange et al., 1985). This study is a direct quantification of shocked serpentine water-loss kinetics.

**RESULTS AND DISCUSSION**

Kinetic information can be obtained from the variation in DSC peak position with heating rate by means of the following analysis, which follows that of Klamt (1957). For a first-order decomposition reaction such as

$$\text{Solid} \rightarrow \text{Solid} + \text{Gas}$$

(2)

the rate of reaction can be expressed as

$$dx/dt = A_0 (1 - x) \exp \left( -E_a/RT \right)$$

(3)

where $x$ is the fraction of Solid 1 that has decomposed at a given time $t$, $A_0$ is the preexponential constant, $E_a$ is the activation energy for the decomposition reaction, $R$ is the gas constant, and $T$ is absolute temperature. The time dependence of the reaction rate during DSC is given by

$$d(\phi)/dt = d(\phi)/dt \left( E_a/RT^2 \right) \exp \left( -E_a/RT \right)$$

(4)

Fig. 6. Variation of preexponential term $A_0$ and activation energy $E_a$ for dehydration of serpentine with peak shock pressure.
Fig. 6. Serpentine decomposition parameters $A_0$ and $E_a$ as a function of $P_{H_2O}$ from Bridle et al. (1967) along with the corresponding parameters for unshocked serpentinite from this study. Solid and dashed lines are exponential fits to the data of Bridle et al. for $A_0$ and $E_a$, respectively.

Thus a plot of ln ($d/T_d^2$) versus $1/T_d$ will have a slope equal to $E_a/R$ and an intercept of $ln (A_0R/kb)$. Figure 4 is such a plot of the DSC data of this study for the serpentine decomposition reaction:

$$\text{MgSi}_2\text{O}_4\text{(OH)}_2 = 3\text{MgO} + \text{SiO}_2 + \text{H}_2\text{O}$$

The solid products are written as $3\text{MgO} + \text{SiO}_2$ instead of forsterite plus enstatite ($\text{Mg}_2\text{SiO}_4 + \text{MgSiO}_3$) because recrystallization may not take place on the time scale of the analysis. The figure shows that for each sample (shocked or unshocked) the data fall on a straight line, and therefore values of $A_0$ and $E_a$ can be obtained using equation (5). These data are listed in Table 2. As shown in Fig. 5, values of $A_0$ are 5 to 6 orders of magnitude lower and values of $E_a$ are nearly a factor of 2 lower for the shocked serpentine relative to the unshocked material. There is no apparent systematic variation in $A_0$ or $E_a$ with shock pressure. Thus, even though the impact experiments were carried out under conditions that inhibit impact-induced devolatilization, the shocked materials exhibit greatly different dehydration kinetics from the unshocked mineral.

Serpentine dehydration kinetics under varying water vapor pressure conditions have been studied by Bridle et al. (1967). They showed that the rate of serpentine dehydration is strongly dependent on ambient $P_{H_2O}$. Surface layers of chemically adsorbed $H_2O$ inhibit the dehydration reaction. The thermal analyses of this study were performed in a nitrogen stream (flow rate ~20 ml/min) with no direct control of $P_{H_2O}$. Figure 6 is a plot of $A_0$ and $E_a$ versus $P_{H_2O}$ from the results of Bridle et al. (1967) and the results for unshocked serpentinite of this study. Our results are consistent with those of Bridle et al. (1967) and indicate an ambient $P_{H_2O}$ during thermal analysis of approximately 0.2 to 0.3 mm Hg (~2.5 to $4 \times 10^{-5}$ bar). This experimental value of $P_{H_2O}$ may be caused by released $H_2O$ trapped in the interstices of the reacting powder. Note that estimates of $P_{H_2O}$ may be caused by released $H_2O$ trapped in the interstices of the reacting powder. Note that estimates of $P_{H_2O}$ on the present-day Martian surface lie between about 6 x $10^{-5}$ bars (the vapor pressure of ice at 273 K) and 4 x $10^{-8}$ bars (Goody, 1976) with an observed maximum of 3 x $10^{-5}$ bars (Furness et al., 1976). Thus it is reasonable to apply our results directly to calculations concerning the Martian surface.

Figure 7 is a plot of the logarithm of the relative first order rate constant (shocked versus unshocked) versus reciprocal temperature, where the rate constant $k$ is given by

$$k = A_0 \exp (-E_a/RT)$$

Note that a reduction in values of $A_0$ yields a reduction in dehydration rate, whereas a reduction in activation energy $E_a$ results in an increase in dehydration rate. The net effect of the lowered values of $A_0$ and $E_a$ is a rate of dehydration for shocked serpentinite greater than for unshocked serpentinite. Over the temperature range in which the dehydration occurs during DSC analysis, about 500° to 800°C, dehydration of shocked serpentinite proceeds at a rate up to about 10 orders of magnitude greater than that of unshocked serpentinite. The rate enhancement is most pronounced at lower temperatures. Extrapolation to the temperature of the surface of Mars (about 170° to 500°C) yields a rate of dehydration of shocked serpentinite 20 to 30 orders of magnitude greater than for unshocked serpentinite.

Fig. 7. Logarithm of the relative rate constant for dehydration of shocked compared to unshocked serpentinite, log $(A_0R/k)$ versus reciprocal temperature.
The large shock enhancement of the bulk serpentinizing dehydration rate caused by the large number of lattice defects (and, hence, weakened chemical bonds) introduced during shock deformation and by the increase in surface area caused by shock comminution of the starting material. The relative magnitudes of these effects on the reaction rate are not differentiated in this study. Note that the rate of reaction of a gas with a solid, i.e., the reverse of reaction (2), will also be enhanced by these same shock effects, although to what extent cannot be determined from results of this study. However, these results indicate that the rate of attainment of chemical equilibrium will be greatly enhanced in shocked materials.

The effects of shock enhancement of solid-gas reaction rates are important in planetary development. Atmosphere-lithosphere interactions will be rapid on a planetary surface strongly affected by impacts. Chemical buffering of atmospheric speciation during planetary accretion will be facilitated. Thus, even in the very early, very cold stages of accretion, protomantid-surface reaction rates would very likely have been sufficient to maintain chemical equilibrium with the shocked near-surface rocks. Shock enhancement of reaction rates will also have a significant influence on chemical weathering of present-day planetary surfaces, as has been suggested by Bodough et al. (1980, 1986), Bodough and Ogun (1987) investigated the enhancement of dissociation rates of shocked minerals. On the Martian surface, hydroxyl-free magnesium silicates are metastable with respect to magnesium carbonate (magnesite) plus quartz plus MgO (Greenwood, 1978). Gooding points out that on Mars, reactions between atmospheric gases and solid minerals rather than between aqueous solutions and minerals may control the rates and products of chemical weathering. He postulates that metastable mineral assemblages (i.e., hydroxyl-free magnesium silicates) might occur as intermediates during the weathering of igneous rocks and then remain unreacted because of low reaction rates. The results of this study suggest that any areas that have undergone impact, attainment of an equilibrium mineral assemblage is probable.

CONCLUSIONS

Values of both the preexplosive term A and the activation energy E, for the rate constant for dehydration of serpentine are greatly reduced by impact. Net dehydration rates are orders of magnitude higher for shocked samples compared to unshocked samples even though the shock experiment was performed in assemblies that inhibited impact-induced devolatilization. At temperatures of the Martian surface, the decomposition rate of shocked serpentine is 20 to 80 orders of magnitude greater than that for unshocked material. Thus, planetary surfaces that are strongly affected by impacts will rapidly reach chemical equilibrium with the atmosphere. Buffeting of atmospheric composition by surface materials would have occurred during even the earliest, coolest stages of accretion. Long term persistence of metastable mineral assemblages is very unlikely on highly impacted surfaces.

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