

EFFECT OF SHOCK ON THE KINETICS OF THERMALLY-INDUCED DEHYDRATION OF SERPENTINE; James A. Tyburczy, Department of Geology, Arizona State University, Tempe, AZ 85287 and Thomas J. Ahrens, Seismological Laboratory, California Institute of Technology, Pasadena, CA 91125.

It has been suggested that, in addition to causing the immediate loss of some of the structurally bound water in serpentine, impact causes a reduction in the strength of the bonds holding the remaining hydroxyl groups in the solid (1,2). Evidence for this hypothesis includes infrared spectroscopic analyses of shocked material that show a broadening of peak width and a decrease in peak intensity of the 3690 cm^{-1} band associated with OH-stretching vibration modes (2). We report here the results of a calorimetric study of shocked serpentine performed to determine the activation energy for dehydration of the shocked material.

The impact experiments were performed using the 40 mm powder gun at the California Institute of Technology. The stainless steel sample chamber assembly employed was a scaled-up version of that used in previous solid recovery experiments on the 20 mm gun (2). The samples consisted of 0.7 to 1.0 g of powdered serpentine (lizardite) pressed to a density of approximately 2.12 g/cm^3 (15% porosity). An important difference between the experiments reported here and previous work is that although an attempt was made in this work to provide venting in order to permit the escape of released gases, the large volume of sample shocked apparently prevented the escape of released gases. Therefore little or no devolatilization of the serpentine occurred in any of the shots, although approximately 10 to 40% of the H_2O was lost from porous samples shocked to the same pressures in vented assemblies (4). This result is consistent with previous findings concerning the effects of sealed versus vented sample assemblies and with calculations of the effects of ambient volatile partial pressure on the extent of shock-induced devolatilization (2,3,5). Nevertheless, the calorimetric analysis of the shocked material clearly shows increased ease of thermal dehydration over the unshocked material (see below).

Differential scanning calorimetry (DSC) on approximately 20 mg aliquots of shocked and unshocked material was performed in a N_2 atmosphere using a Mettler Thermoanalyzer 2000C. Figure 1 shows the DSC curves obtained using heating rates of 2, 5, 10, and 25 K/min for unshocked serpentine and for serpentine shocked to an initial shock pressure of 7.6 GPa. The endothermic (downward) peak occurring at temperatures between 600 and 700° is the water-loss peak. The results show that for the same heating rate, there exists a 50 to 70 degree reduction in the temperature of the water-loss peak for the shocked material relative to the unshocked material. Furthermore, there is a systematic variation in the peak position with heating rate. This variation indicates that attempts to glean kinetic information from DSC or thermogravimetric curves without consideration of heating rate effects are seriously in error (1,2). For a first-order solid decomposition reaction, the relationship between the heating rate ϕ , the temperature of the maximum of the water-loss peak T_m , and the activation energy for dehydration E_a is given by (6)

$$d \ln (\phi/T_m^2)/d (1/T_m) = -E_a/R \quad (1)$$

Thus, a plot of ϕ/T_m^2 versus $1/T_m$ is a straight line with slope $-E_a/R$. In Figure 2 the results of this study are plotted. The unshocked serpentine results yield an activation energy of 340 kJ/mole, which is in reasonable agreement with literature values of 285 kJ/mole under vacuum and 373 kJ/mole under 1.2 mm vapor pressure of H_2O (7). The shocked samples give activation energies of 220 to 235 kJ/mole, independent of shock pressure. The activation energy for dehydration of shocked serpentine is 30-35% lower than that of unshocked serpentine.

The results of this study indicate that the kinetics of dehydration of shocked serpentine are significantly more rapid than for unshocked serpentine, even when the shock occurs under conditions in which devolatilization is inhibited or prevented. Therefore, the rate of dehydration (in a subsequent thermal event) of buried or surficial hydrous minerals that have been shocked will be greater than for minerals that have not been shocked. Thus, impact processes not only directly cause the devolatilization of surface materials, but also enhance the rate of volatile loss of subsurface materials, if suitable temperature conditions exist. These results also suggest that rates of chemical weathering of surface materials are greatly enhanced in shocked materials.

DEHYDRATION KINETICS OF SHOCKED SERPENTINE

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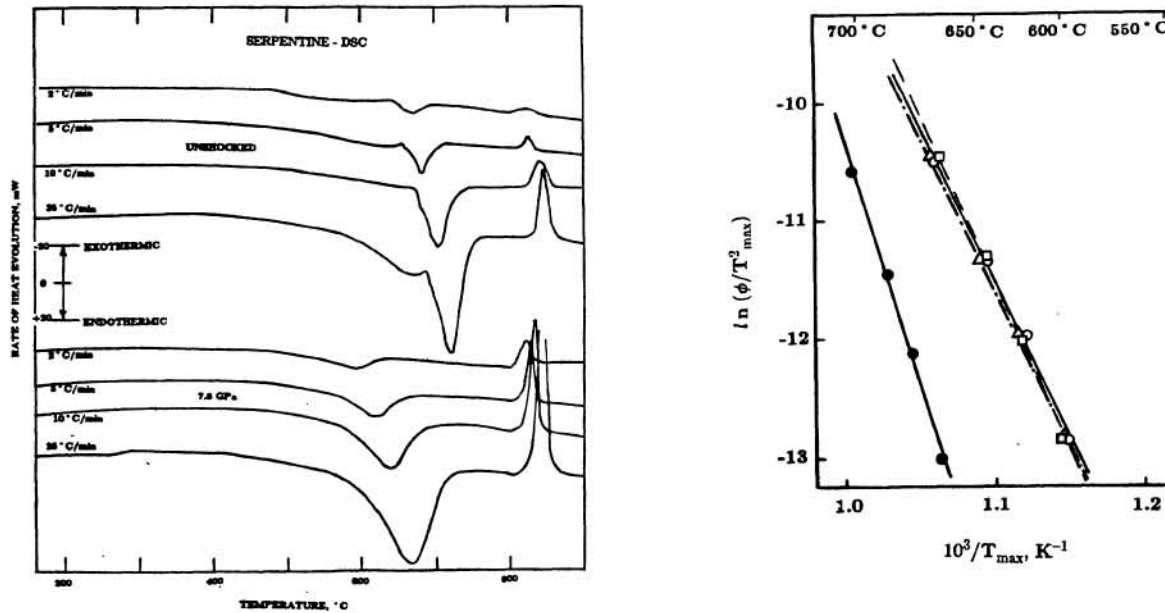


Figure 1. Differential scanning calorimetry (DSC) curves for unshocked serpentine and serpentine shocked to 7.6 GPa (Shot 692). Deflection downward represents an endothermic reaction. The different lines represent results for different heating rates. Sample mass for each run is approximately 20.6 mg. Negative deflection between 600-720 °C is the water-loss peak. Positive deflection at about 800 °C is an undetermined solid-solid reaction.

Figure 2. Plot of $\ln(\phi/T_m^2)$ vs. T_m^{-1} for unshocked and shocked serpentine. Filled circles and solid line, unshocked serpentine; open circles and solid line, shot 692 (7.6 GPa); open squares and dashed line, shot 693 (9.4 GPa); open triangles and dash-dot line, shot 694 (12.5 GPa). Lines represent linear least-squares fits to the data for each shot.

Table 1. Experimental Results

Shot number	Initial density, g/cm ³	Projectile Velocity, km/s	Initial Shock Pressure, GPa	DSC heating rate, K/min	T _{max} of water-loss peak, °C	Activation Energy, kJ/mole
unshocked	—	—	—	25	722	340
				10	699	
				5	684	
				2	667	
692	2.13	1.07	7.6	25	670	220
				10	641	
				5	619	
				2	598	
693	2.17	1.25	9.4	25	669	235
				10	641	
				5	620	
				2	600	
694	2.09	1.55	12.5	25	673	220
				10	643	
				5	621	
				2	600	