

IMPACT-INDUCED DEVOLATILIZATION AND HYDROGEN ISOTOPIC FRACTIONATION OF SERPENTINE: POSSIBLE IMPLICATIONS FOR PLANETARY ACCRETION; James A. Tyburczy<sup>1</sup>, R.V. Krishnamurthy<sup>2</sup>, Samuel Epstein<sup>2</sup>, and Thomas J. Ahrens<sup>3</sup>, <sup>1</sup>Department of Geology, Arizona State University, Tempe, AZ 85287, <sup>2</sup>Division of Geological and Planetary Sciences 170-25, California Institute of Technology, Pasadena, CA 91125, <sup>3</sup>Seismological Laboratory 252-21, California Institute of Technology, Pasadena, CA 91125.

**Introduction.** Impact-induced devolatilization of volatile-bearing rocks and minerals is an important process influencing planetary accretion, early atmosphere formation, and chemical weathering of planetary surfaces (1,2). Previous experimental investigations of this process have focussed on the shock pressure (impact velocity) dependence of the extent of impact-induced devolatilization in hydrous minerals, carbonates, and meteorites (3,4,5) and on the shock enhancement of chemical reactivity of silicates (6,7). We have performed a direct comparison of the two experimental techniques for measuring impact-induced devolatilization, namely the gas-recovery and solid-recovery techniques. In addition, we have examined the hydrogen isotopic composition of the gaseous products of impact-induced devolatilization of serpentine.

**Experimental Details.** The material studied was a magnesium end member lizardite serpentine with a density of 2.50 g/cm<sup>3</sup> and  $\delta D_{SMOW}$  of -77 per mil. Solid-recovery impact-induced devolatilization experiments were performed on the 20 mm powder gun at Caltech using vented, stainless steel sample assemblies and thermogravimetric analysis of the recovered material as described previously (4,5). Powdered samples of about 85% of the bulk density were shocked. Gas-recovery experiments were performed using an assembly that retained the shock-evolved gases (8). After impact the trapped gases were transferred to a vacuum system for manometric and isotopic analysis. An empty assembly was impacted in the same manner as the sample-bearing experiments. Manometric analysis of the recovered gases was performed using standard techniques (9). Recovered gases were separated into four fractions; H<sub>2</sub>, other gases not condensible in LN<sub>2</sub>, CO<sub>2</sub>, and H<sub>2</sub>O. The results of the manometric and isotopic analyses for the blank- and sample-derived gases are listed in Table 1. The blank yielded amounts of H<sub>2</sub> and H<sub>2</sub>O insufficient for accurate mass spectrometric determination of D/H ratios. These amounts were subtracted from the total H<sub>2</sub> plus H<sub>2</sub>O recovered in determining the fraction of initial H<sub>2</sub>O volatilized during the impact. Shock pressures were calculated using a one-dimensional impedance match solution (5).

**Results and Discussion.** For shock to 17.5 GPa, the only H-containing gas evolved in significant amounts is H<sub>2</sub>O. For higher shock pressures, both H<sub>2</sub> and H<sub>2</sub>O are found in the recovered gases (Table 1). We postulate that the H<sub>2</sub> in the recovered gas is a result of oxidation of iron metal in the experimental assembly. The total H<sub>2</sub>O driven from serpentine is calculated as the sum of the H<sub>2</sub>O plus H<sub>2</sub> collected, less the blank. The actual H<sub>2</sub> content of the noncondensable recovered gas fraction was not determined for each experimental shot. On the basis of the results for shots 911 and 915, we assume that approximately 1/2 of the total noncondensable gases recovered is H<sub>2</sub>. Thus, for the other shots, the total H<sub>2</sub> plus H<sub>2</sub>O recovered is calculated as the sum of the H<sub>2</sub>O recovered and 1/2 of the noncondensable gases recovered. Figure 1 compares the impact-induced water loss for porous serpentine as a function of peak shock pressure determined by the gas- and the solid-recovery methods. In the pressure region of overlap, the agreement is excellent.

The hydrogen isotopic composition  $\delta D$  of the gaseous H<sub>2</sub>O recovered from shock to 17.5 GPa is nearly identical to that of the starting material (Table 1). For shock to 23 and 26 GPa, respectively, the recovered gases have a significantly lower  $\delta D$  than the starting serpentine, about -95 per mil for the H<sub>2</sub>O and -220 for the H<sub>2</sub>. The hydrogen fractionation between the recovered H<sub>2</sub>O and H<sub>2</sub> indicates gas equilibration temperatures of about 1100 K (10). Calculated shock temperatures lie between 600 K and 770 K. This result suggests that shock-induced devolatilization is initiated at localized sites of thermal energy deposition, such as 'shear instability' regions (11).

The calculated per mil gas-solid residue fractionations  $\Delta_{gas-residue}$  ( $\Delta_{gas-residue} = 10^3 \ln \{(1000 + \delta D_{gas}) / (1000 + \delta D_{residue})\}$ ), are 5, -61, and -101 for shots 867, 911, and 915, respectively. Over the temperature range 300-1100 K,  $\Delta_{H_2O-mineral}$  values generally lie between -50 and +20 per mil (12). H<sub>2</sub>O-silicate melt per mil fractionations generally lie above +20 per mil (13). The  $\Delta_{gas-residue}$  values for shots 911 and 915 lie well outside the range of equilibrium values for H<sub>2</sub>O-mineral or H<sub>2</sub>O-melt isotopic fractionations, suggesting that the observed gas-residual solid isotopic fractionations are the result of kinetic control.

**Conclusions.** The influence of impact-induced hydrogen isotopic fractionation of hydrous silicates during accretion on planetary isotopic compositions depends on the mass fraction of the planet accreted in an impact velocity regime in which partial devolatilization of incident and impacted material occurs. For very high impact velocities, complete devolatilization occurs and no isotopic fractionation would take place. For an Earth-sized planet, partial devolatilization on impact occurs over a small range of mass accreted, a few per cent at most (5). For a Mars-sized planet, partial devolatilization would occur over about 20 per cent of the planetary mass accreted.

Long term persistence of the impact-induced isotopic fractionation signature would further require isolation of the gas and solid isotopic reservoirs, either by rapid burial of the solid shocked material or by rapid planetary escape of the evolved gases. Both of these necessary conditions would be more likely to be met on a Mars-sized or smaller planetary body.

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Table 1. Isotopic results of gas-recovery experiments

Shot Number	Peak Shock Pressure GPa	Recovered Non-condensable Gases $\mu\text{mole}$	Recovered $\text{H}_2$		Recovered $\text{H}_2\text{O}$		Total Recovered $\text{H}_2 + \text{H}_2\text{O}$ as % $\text{H}_2\text{O}$ in Initial Sample
			$\mu\text{mole}$	$\delta\text{D}$ , per mil	$\mu\text{mole}$	$\delta\text{D}$ , per mil	
913	23.7	1.0	0.4	-	1.0	-	
889	17.0	0.2	-	-	0.8	-	BDL
867	17.5	BDL	-	-	6.6	-72	4.2*
875	9.5	18.6	-	-	4.8	-	7.9*
890	11.5	21.0	-	-	1.8	-	4.5*
911	13.0	23.2	4.6	-204	11.2	-93	12.7
915	13.0	26.4	7.5	-238	10.9	-98	11.9

$\delta\text{D} = \{[(\text{D}/\text{H})_{\text{sample}}/(\text{D}/\text{H})_{\text{SMOW}}] - 1\} \times 1000$ ; SMOW, Standard Mean Ocean Water

\* Recovered  $\text{H}_2$  calculated as 1/2 of total non-condensibles

BDL Below detection limit

- Not Determined

Figure 1. Impact-induced water loss as a function of peak shock pressure for 15% porous serpentine. Open symbols, gas recovery method; filled symbols, solid recovery method. Solid line is empirical fit to solid recovery data.

