

ASSESSMENT OF SHOCK EFFECTS ON HORNBLENDE WATER CONTENTS AND ISOTOPIC COMPOSITIONS.

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Introduction

The only samples currently available of Mars, the SNC meteorites, come to Earth via the impact process. In order to use the SNC's to gain insight into the magmatic water budget of Mars, the effect of the impact process on the water contained within the SNC's must be understood. Impact-induced water loss and D enrichment have been proposed to explain the water contents and isotopic compositions of hydrous phases within the SNC's (1). Impact shock experiments on Gore Mountain amphibolite (1) yielded shocked hornblende with D/H ratios 2-4 times greater than that of unshocked hornblende. Further petrographic and analytical studies have been carried out on these samples and other unshocked and shocked samples from the original shock experiment to assess the degree of shock experienced by the samples and measure any shock-induced change in D/H ratio and water content of the hornblende. In addition, a new shock experiment has been done at a higher projectile velocity in an attempt to obtain samples shocked to the same degree as the SNC's. At this time, only the original experimental products have been analyzed.

Petrographic Analysis

In order to petrographically determine the degree of shock the original experimental products (1) experienced during impact, grain mounts were made of hornblende, orthopyroxene and plagioclase aggregates and individual plagioclase grain fragments. All minerals display irregular fractures and undulatory extinction, suggestive of shock pressures on the order of 10 GPa (2). A portion of the plagioclase grains observed in the grain mounts have planar deformation features which are closely and evenly spaced, are from 2-6 μm wide, remain virtually extinct throughout rotation and are associated with areas of undulatory extinction in their respective grains. Such planar deformation features are indicative of shock pressures of 20-30 GPa (2). Other plagioclase grains have greatly reduced birefringence (0.001-0.003) relative to normal plagioclase birefringence (0.007-0.013) (3). Reduced birefringence is observed in plagioclase grains who have experienced shock pressures approaching those required to create maskelynite (30-35 GPa) (4). Overall, the petrographic observations of the shocked Gore Mountain material indicate that while portions of the sample have experienced shock pressures up to 30 GPa, the sample overall has experienced shock pressures of 10 GPa.

Ion Microprobe Analyses

Analytical A set of ion microprobe analyses was carried out on the Cameca IMS 6f at the Department of Terrestrial Magnetism (DTM) at the Carnegie Institute of Washington. The same unshocked and shocked samples studied by (1) were reanalyzed for isotopic compositions and water contents. For measurements of isotopic composition, H_2 interference in the D signal was controlled by using a Cs^+ primary beam rather than an O primary beam. The relative sizes of the H_2 and D signals on the 6f were confirmed by completing a peak scan across the mass 2 range at a mass resolution of 1800. The H_2 signal was 0.15% of the D signal. Before analysis, the sam-

ples were stored in the airlock of the microprobe for a minimum of 24 hours. D and H were measured on both unshocked and shocked samples with no voltage offsets, primary beam currents of 1-3 nA, an un rastered beam of 30 μm diameter, a field aperture of 15 μm , and an energy window of ± 125 V. Charging of the sample was overcome by the use of an electron flood gun. The magnet range was reduced to 0-30 amu and magnet drift, checked periodically during an analysis day, was never greater than 0.001 amu over a 0.01 amu peak width. Before each D and H measurement, the magnet was cycled between the D and H peak positions to eliminate any hysteresis effect from the magnet. In order to determine the instrumental fractionation factor (α_{ins}), the isotopic composition of a standard was measured in concert with that of the unshocked and shocked samples. The standard, Bita Hochee ($\delta\text{D} = -52\text{‰}$, 1.4 wt% H_2O), is a Mg-kaersutite selected because of the similarity of its major element composition to that of unshocked Gore Mountain. The isotopic composition of the standard was measured every 1-7 unknown analyses and α_{ins} 's for each unknown measurement were determined by extrapolating α_{ins} 's between standard measurements. Measured D/H ratios were also corrected for background and dead time of 23 ns. $\pm 2\sigma$ analytical uncertainty in the isotopic data is $\pm 6\text{‰}$. Based on measurements of α_{ins} of amphibole standards of a range of major element compositions, the α_{ins} determined from Bita Hochee is applicable to the Gore Mountain measurements with a $\pm 2\sigma$ accuracy of $\pm 10\text{‰}$ (Hauri, pers. comm., 1998).

Measurement of the water content of the unshocked and shocked samples was carried out on a different day than the isotopic composition measurements. The defocused Cs^+ primary beam was 7 nA and 30 μm in diameter and the field aperture was 8 μm . Water contents were established using a calibration curve containing data from standard amphiboles and hydrous glasses. Uncertainty in the water measurements is $\pm 10\%$ (Hauri, pers. comm., 1998).

Results The isotopic compositions and water contents of the samples measured at DTM show overlap in unshocked and shocked values. Unshocked samples were found to have a wide range in composition, from -59‰ to -109‰ and the shocked samples had a similarly large range, from -68‰ to -107‰ . Water contents of the unshocked samples fell between 1.80 to 2.84 wt% H_2O whereas water contents of the shocked samples ranged from 1.70 wt% to 3.10 wt%.

Mass Spectrometry Analysis

An unshocked and two shocked samples from the original shock experiment (1) were analyzed by volatile extraction and mass spectrometry. The extraction and mass spectrometry were carried out at the California Institute of Technology.

Analytical The same basic procedure was followed for each extraction. The sample was allowed to pump down overnight in the extraction line. Before sample analysis, the system blank was measured by heating the sample crucible for one hour to temperatures approximating that of the peak extraction temperature. During both the blank and sample extractions, the line was opened up to the CuO furnace (600 –

616 °C). Blank yields measured between 0.05 and 0.21 $\mu\text{moles/hour}$. After blank measurement, the sample was inserted into the crucible for single step volatile extraction by pyrolysis. Sample temperatures were increased in 100 °C steps from 500 °C to maximum temperatures between 1390 °C and 1455 °C over 20–30 minutes. CO_2 and H_2O were collected during extraction in a LN_2 slush and CO_2 was separated from H_2O by replacing the LN_2 slush with a dry ice/organic solvent slush. Removal of the dry ice/organic solvent slush allowed the condensed water to pass through a U furnace (793 – 825 °C). Any unreduced water was forced back through the U furnace by movement of the dry ice/organic solvent trap. The H_2 was collected with a Toeppler pump and the yield was measured via manometry. A transfer ampoule attached to the extraction line was used to transport the H_2 from the line to the mass spectrometer. Estimated uncertainties in the water contents are $\pm 0.3 \mu\text{moles}$ and in the δD values are $\pm 2\%$ (5).

Before the extraction and mass spectrometric analyses of the unknowns, an extraction and isotopic measurement of a standard was conducted. The standard, NBS30, is a biotite with $\delta\text{D} = -64\%$ and 3.7wt% H_2O (Newman, pers. comm., 1997). The measured isotopic composition was -60.6‰ and the measured water content was 3.43 wt% H_2O .

Results While increasing the temperature of the sample for extraction, the amount of gas released in each temperature step was noted. A single spike in the release pattern was observed for all unknowns and the spike occurred at temperatures near the peak extraction temperature, indicating the absence of an adsorbed water component (Newman, pers. comm., 1997). The single unshocked grain yielded a $\delta\text{D} = -19.5\%$ and a water content of 2.13 wt% H_2O . Both shocked aliquots consisted of multiple grains and the grains of neither aliquot had the characteristics of the most highly shocked grains (powdery, friable). The first set of shocked grains yielded a $\delta\text{D} = -44.8\%$ and 1.86 wt% H_2O and the second set had a $\delta\text{D} = -42.1\%$ and 1.85 wt% H_2O .

Discussion

The δD 's of the shocked samples measured to date by the ion microprobe fall within the range of the unshocked δD 's. The microprobe data also show that the range of water contents in the shocked samples extends to higher and lower water contents than the range defined by the unshocked samples. The microprobe data overall do not indicate that a consistent water loss or D enrichment occurred via the applied experimental shock (10-30 GPa). The mass spectrometry data also show no isotopic enrichment in the shocked samples relative to the unshocked sample for the original experimental material. However, the extraction data do demonstrate a consistent water loss (0.3 wt% H_2O) in the shocked samples relative to the unshocked samples. These observations are based on only one unshocked sample analysis.

The difference between the isotopic compositions of the unshocked Gore Mountain hornblende obtained from mass spectrometry and from the ion probe is striking yet not well understood. There are several potential contributing factors to the measured differences. Any error in the α_{ins} applied to the Gore Mountain samples stemming from compositional differences between the sample and standard would lead to an incorrectly calculated δD for the Gore Mountain samples.

However, the spread in α_{ins} 's determined from standards with a wide range in major element compositions is 70‰ (Hauri, pers. comm., 1998). While this variation is equivalent to the differences in δD between the mass spectrometry and ion probe analyses, the compositional difference between Beta Hochee and Gore Mountain is significantly smaller than the compositional range of the measured standards. Thus, the complete difference in ion probe and mass spectrometric δD values is not likely due to differences between the standard and sample. Another potential factor is hydrothermal alteration of the Gore Mountain sample. Alteration products are observed in thin section affecting only orthopyroxene but suggest that the δD of the hornblende may have been altered by the same fluid that produced the orthopyroxene alteration. The difference in the scale of measurement in mass spectrometry and in the ion probe (bulk vs. microscopic) as well as the lack of multiple unshocked sample analyses via mass spectrometry may also have played a role in the measured differences in δD .

Keeping in mind the mass spectrometry and ion probe measurement differences, the relationship between the measured δD and water contents and the experimental shock pressure can be considered. As stated above, the data do not demonstrate a consistent reduction in H_2O content or increase in δD in the samples shocked to 10-30 GPa. Rather than discounting impact-induced water loss or D enrichment, the results suggest that at the shock pressures achieved during the original experiment, water loss and D enrichment were not large enough to overcome the natural variations in the unshocked δD and H_2O content.

In light of the current results, it is difficult to understand the data of (1) which showed large and consistent increases in D/H and decreases in H^{20}Si . Possible explanations for the results include variable analysis conditions, incomplete energy filtering of the H_2 signal from the D signal and lack of standard use. Adsorbed water contributing to the mass 2 signal via H_2 is not likely the cause of the measured ratios because low-temperature spikes in the release patterns obtained in the volatile extractions of the current work are not observed.

With respect to the SNC meteorites, the original experimental products have suffered lower overall and peak pressures than most of the SNC's, as they commonly contain maskelynite (6). Thus, impact-induced water loss and D enrichment may have occurred in the SNC's, but the degree to which the meteorites may have been affected remains experimentally unconstrained. A second shock experiment has been carried out on another Gore Mountain sample in which the projectile velocity was increased relative to that in the original shock experiment (4.97 km/s vs. 5.78 km/s). The new experimental product will be studied petrographically and compositionally in order to measure any impact-induced water loss or D enrichment produced by the higher experimental shock pressure.

References [1] Minitti et al. (1997) *LPSC XXVIII*, 959-960. [2] Stofler et al. (1991) *GCA*, 55, 3845-3867. [3] Nesse W.D. (1991) *Introduction to Optical Mineralogy*, 2nd ed., New York: Oxford University Press, Inc., 268-277. [4] Ostertag R. (1983) *Proc. LPSC XIV.; JGR*, 88, B364-B376. [5] Leshin et al. (1996) *GCA*, 60, 14, 2635-2650. [6] McSween H.Y., Jr. (1994) *Meteoritics*, 29, 757-779.