Final Progress Report

High-pressure minerals in meteorites: Constraints on Shock Conditions and Duration

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1. Research Objectives

The objective of this research was to better understand the conditions and duration of shock metamorphism in meteorites through microstructural and microanalytical characterization of high-pressure minerals.

A) Continue to investigate the mineralogy and microstructures of melt-veins in a suite of chondritic samples ranging from shock grades S3 through S6 to determine how the mineral assemblages that crystallize at high-pressure and are related to shock grade.

B) Investigate the chemical, mineralogical, and microstructural heterogeneities that occur across melt veins to interpret crystallization histories.

C) Use static high-pressure experiments to simulate crystallization of melt veins for mineralogical and textural comparisons with the melt veins of naturally shocked samples.

D) Characterize the compositions and defect microstructures of polycrystalline ringwoodite, wadsleyite, majorite, $(Mg,Fe)SiO_3$-ilmenite and $(Mg,Fe)SiO_3$-perovskite in S6 samples to understand the mechanisms of phase transformations that occur during shock. These results will combined with kinetic data to constrain the time scales of kinetic processes.

E) Investigate the transformations of metastable high-pressure minerals back to low-pressure forms to constrain post-shock temperatures and estimates of the peak shock pressure.

Of these objectives, we have obtained publishable data on A, B and D. I am currently doing difficult high-pressure melting and quench experiments on an L chondrite known as Mbale. These experiments will provide additional constraints on the mineral assemblages that are produced during rapid quench of an L chondrite at pressures of 16 to 25 GPa. Results from published or nearly published research is presented below. Lists of theses, dissertations and publications are given below.

2. Research Results

Melt-vein crystallization pressure versus calibrated shock pressure

The characterization of the minerals that crystallize from shock-induced melt veins and pockets and their use for determining pressure has been the primary aim of our research. Since we determined that the melt-vein assemblage in Sixiangkou (Chen et. Al 1996) could constrain the crystallization pressure, we have been evaluating how the

crystallization pressure is related to the shock pressure determined from conventional shock features (Stöffler et al., 1991). A paper is written on these results, which will be submitted in 2004. Two papers on the Umbarger L6 chondrite have been published.

We have investigated a suite of shock-vein bearing L chondrites, ranging from shock stages S3 to S6. The mineral assemblages combined with phase equilibrium data are used to constrain the crystallization pressures. In doing this we do not assume chemical equilibration during crystallization, but rather use the pressure stabilities of the minerals and mineral assemblages to constrain the crystallization pressure. The goal is to see how crystallization pressures are related to the shock stage and the pressures inferred from the pressure calibration of shock features. Seven L6 chondrites were investigated using FESEM and TEM techniques: Tenham (S6), Umbarger (S4*-S6), Roy (S3*-S5), Ramsdorf (S4), Kunashak (S4), Nakhon Pathon (S4) and La Lande (S4). The melt veins of the Tenham include majorite and magnesiowüstite in the center of the melt vein, and ringwoodite, akimotoite, vitrified silicate-perovskite and majorite in the edge of the vein. Both mineral assemblages indicate crystallization pressure ~22-25 GPa. The melt veins of the Umbarger include: ringwoodite, akimotoite and clinopyroxene in vein matrix, and Fe_2SiO_4-spinel and stishovite in SiO_2-FeO rich local area of the melt vein. The pressure stabilities of these minerals meat at about 18 GPa, but it is possible that crystallization started at 25 GPa and continued below 18 GPa. The melt veins of Roy include ringwoodite plus majorite, indicating pressure ~18 GPa; The melt veins of Ramsdorf and Nakhon Pathon contain olivine and clinopyroxene, indicating pressure less than 15 GPa; The melt veins of Kunashak and La Lande include albite and olivine, indicating crystallization at low pressure (<2.5 GPa), presumably after shock pressure release. These crystallization pressures can be grouped into three pressure regions (Fig.1). Based upon the assemblages observed, crystallization of shock veins can occur before, during or after pressure release. When the assemblage consists of high-pressure minerals and that assemblage is constant across a melt vein or pocket, the crystallization pressure was nearly constant and represents the equilibrium shock pressure. Equilibrium shock pressures inferred from the mineralogy of shock-induced melt veins are all $\geq$25 GPa, suggesting that the pressure calibration of Stöffler et al. (1991) for S6 (> 45-55 GPA) is too high by a factor of two for highly shocked (S6) samples.

The Umbarger L6 chondrite, has a previously undocumented set of high-pressure minerals in shock-induced melt veins that result from heterogeneities in the shock induced melt and metastable crystallization upon quench. High-pressure minerals were identified with TEM using selected-area electron diffraction, and energy-dispersive X-ray spectroscopy. Ringwoodite (Fa_{30}), akimotoite ($En_{11}Fs_{89}$), and augite ($En_{42}Wo_{33}Fs_{25}$) were found in the silicate matrix of the melt vein, representing the crystallization from a silicate melt during the shock pulse. Ringwoodite (Fa_{27}) and hollandite-structured plagioclase were also found as polycrystalline aggregates in the melt vein, representing solid-state transformation or melting with subsequent crystallization of entrained host-rock fragments in the vein. In addition, Fe_2SiO_4-spinel (Fa_{66}-Fa_{99}) and stishovite crystallized from a FeO-SiO_2-rich zone in the melt vein, which formed by shock melting of preexisting FeO-SiO_2-rich material that had apparently formed by alteration and metasomatism prior to the impact event that caused the shock. Based on the pressure stabilities of the high-pressure minerals, ringwoodite, akimotoite and Ca-clinopyroxene, the melt pocket crystallized at approximately 18 GPa or crystallization occurred during

very slow pressure release from ~ 25 to 18 GPa. The Fe_2SiO_4-spinel + stishovite assemblage in the FeO-SiO_2-rich melts is consistent with crystallization of the melt-vein matrix at the pressure up to 18 GPa. The crystallization pressure of ~ 18 GPa is much lower than the 45 – 90 GPa pressure one would conclude from the S6 shock effects in melt veins and pockets (Stöffler et al. 1991) and somewhat less than the 25-30 GPa inferred from S5 shock effects (Schmitt 2000) found in the bulk rock.

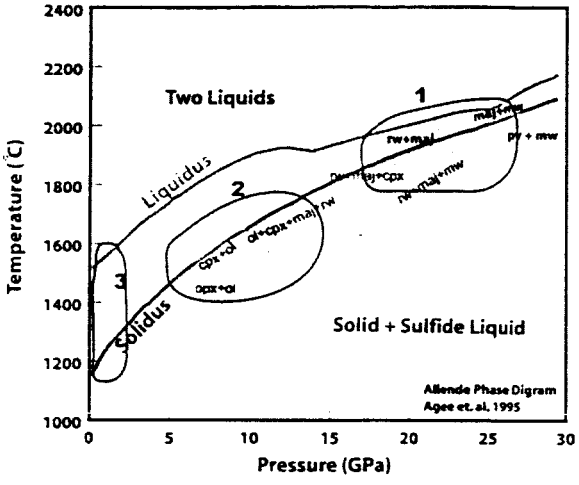

Fig. 1. Three crystallization pressure regions of the shock-induced melt veins are illustrated on a simplified version of the Allende phase diagram (Agee et al. 1995). (1) Crystallization region for Tenham (S6), Roy (S3-S5*) and Umbarger (S4-S6*). (2) Crystallization region for Ramsdorf (S4) and Nakhon Pathon (S4). (3) Crystallization region for Kunashak (S4) and La Lande (S4). ol = olivine, cpx = clinopyroxene, rw = ringwoodite, maj = majorite, mw = magnesiowüstite, pv =perovskite.

Stishovite and post-stishovite polymorphs of SiO_2 in Shergotty

Work on the high-pressure polymorphs of silica in Shergotty was started in the previous grant cycle, but an additional paper has been written and published in this cycle. This paper summarizes the Shergotty results and addresses some of the questions raised by the various workers in this area. We have identified two post-stishovite SiO_2 polymorphs of silica in the Shergotty meteorite by reflected light microscopy, Field Emission Scanning Electron Microscopy, x-ray diffraction and transmission electron microscopy (TEM). Prismatic and wedge-shaped grains of the original accessory tridymite (or cristobalite) in the Shergotty meteorite were densified during a major impact event on the SNC (Shergottite-Nakhlite-Chaissingite) parent body and inverted to multiphase assemblages of several post-stishovite polymorphs. We identified an orthorhombic and a monoclinic post-stishovite silica polymorph, respectively. TEM investigations of the grain containing the orthorhombic polymorph revealed an α-PbO_2-like phase that could be assigned to either *Pnc2* (with the cell parameters: a = 4.55 ± 0.01 Å, b = 4.16 ± 0.03 Å, c = 5.11 ± 0,04 Å), or *Pbcn* space group and dense SiO_2 glass. The x-ray diffraction pattern of the second grain revealed a polymorph with a monoclinic lattice with the space group $P2_1/c$, that is related to the baddeleyite (ZrO_2) structure with the cell parameters: a = 4.375(1) Å, b = 4.584(1) Å, c = 4.708(1) Å, □= 99.97(3), ρ=

4.30(2) gm/cm^3. The grain also contains the α-PbO_2 like phase, stishovite and dense silica glass. TEM-SAED data from this grain revealed the presence of the α-PbO_2-like SiO_2 polymorph, stishovite, secondary cristobalite, and dense silica glass. The coexistence of several high-density polymorphs and dense silica glass in the same grain suggests that several post-stishovite phases were formed during the shock event in Shergotty. Some of these polymorphs were highly unstable and vitrified, presumably in the decompression stage. Based on diamond anvil experiments on cristobalite a peak shock pressure in excess of 40 GPa could be deduced.

Kinetic effects and loading path during shock

Many of the shock effects observed in rocks and minerals are thermally activated processes, which are dependent on both the duration of the shock pulse and the shock temperature. This poses problems for the use of experimentally shocked samples for estimating shock pressures in nature because the duration of such experiments is many orders of magnitude shorter than in nature and the temperature of shock experiments tends to be low. The shock temperature of a sample is dependent on the average shock impedance of the sample and the loading path of shock compression. Most shock-recovery experiments are done in stainless-steel containers that produce high pressures by reverberation of shock waves. This reverberation technique results in a reflected loading path that influences the final temperature of the sample during shock. During the grant period, I worked with Dr. Emma Bowden, a Ph.D. candidate from University College London at the time, to investigate the dependence of shock metamorphic features in quartz as a function of the loading path. This work has not yet been published, but it contributed to the Ph.D. dissertation of Dr. Bowden and she is currently preparing a manuscript for publication.

Samples of porous quartz with a density of 1.42 cc/g were experimentally shock loaded via a variety of direct and reflected loading paths using the single stage powder gun a Tokyo Institute of Technology. Loading paths in the sample material were varied by using materials with a range of shock impedances as the sample containers. For example Polyethylene has a matched impedance with the sample material and produced a single shock-loading path in the sample. Stainless steel, a traditionally used sample container material, has a much higher shock impedance than the porous quartz, with the result that peak pressure in the sample is reached via a sequence of shock reflections. Shock compression is an irreversible process. There is a net gain in internal energy of the specimen as a result of shock compression and release to ambient pressure. The magnitude of this gain in net internal energy depends on loading path. Samples shocked to the same peak pressure via different loading paths can have very different internal energy gains.

Shock conditions in the samples were characterized by calculated loading path and peak pressure, peak pressure duration and calculated net internal energy increase. The shock features formed by shock metamorphism were examined using optical microscopy, X-ray diffraction and transmission electron microscopy. A number of shock metamorphic features were found to be sensitive to loading path rather than to peak shock pressure. That is, the features were evident at relatively low peak pressures in samples that experienced a large increase in net internal energy, whereas much higher peak pressures

were required to produce the same features in samples that experienced smaller increases in net internal energy. These loading path-sensitive features include PDF formation parallel to the {2 1 10} plane, spatial density of PDFs, appearance of crystalline material within PDFs, presence of amorphous silica at grain boundaries, and presence of amorphous silica with grains. There is a strong indication that the pressures of formation of other orientations of PDFs and 'ladder structure' PDFs are also dependent on the net internal energy increase of the sample. These results imply that it may not be appropriate to use shock pressure "calibrations" determined in laboratory reflected shock loading experiments to evaluate the pressure of samples from natural impact craters. The use of the reverberation technique for calibrating shock features results in an over estimate of the shock pressure.

Distribution of high-pressure minerals in and around melt veins

We also investigated a very interesting L6 chondrite, RC106, that contains a large shock-induced melt vein full of high-pressure minerals. This sample contains very large ringwoodite grains and clearly observed transformation of the vein-wall regions that allowed us to investigate the distribution of high-pressure minerals. The aim of this research was to test our hypothesis that the solid-state transformation of minerals in and around melt veins is driven by the locally high temperatures and not by a heterogeneous pressure excursions. This sample also provided a very wide shock vein for use in constraining the duration of shock-vein quench. This study formed the M.S. thesis of Mrs. Carrie Aramovich-Weaver, who graduated in May 2003. A manuscript is written and should be submitted in 2004.

Previously, the apparent heterogeneous distribution of high-pressure phases as melt-vein inclusions was used to argue for very localized pressure heterogeneities known as "pressure excursions" that provided the apparently very high (45-90 GPa) pressures required for the formation of ringwoodite. The concept of pressure excursions has led to various models to explain local pressure peaks, including a model of bubble formation and subsequent cavitation (Spay, 1998). Our findings suggest that the distribution of high-pressure minerals such as ringwoodite, as melt-vein inclusions, is homogeneous despite any apparent optical heterogeneity. This homogeneity is consistent with the formation of high-pressure polymorphs being thermally controlled and thereby not requiring mechanisms of local pressure spikes. Using the melt-vein matrix mineralogy and relevant phase equilibrium data from static high-pressure experiments, crystallization conditions were estimated for the melt vein in RC106. The results suggest the 1.3-mm wide melt vein crystallized at approximately 22-25 GPa and 2200-2400° C. A one-dimensional finite-element heat flow calculation was performed to estimate a cooling time for the thick melt vein.

Thermal modeling of melt-vein quench and P-T-t histories during shock

At the end of this funding period and in the beginning of the subsequent funding period, a primary goal of our research has been to combine our use of melt vein mineralogy to determine crystallization pressures, with thermal modeling to constrain the history of melt-vein crystallization. This provides information on the P-T-t history of the melt veins as well as providing minimum values of the shock-pulse duration. We have applied this approach to both Tenham and RC106. These results have not been published

yet, but they have been presented at meetings and manuscripts are written which will be submitted in 2004.

The microtexture and mineralogy of a 580 μm wide melt vein of the Tenham L6 chondrite were investigated using FESEM and TEM to understand the shock conditions. The melt vein consists of a matrix of silicate plus metal-sulfide grains that crystallized from the melt, and sub-rounded fragments of the host chondrite that have been enclosed in the melt and transformed to polycrystalline high-pressure silicates. Two different textures and mineral assemblages occur in the vein matrix from the edge to the center. The 30 μm-wide vein edge consists of vitrified silicate perovskite + ringwoodite + akimotoite + majorite with minor metal-sulfide. The 520 μm wide vein center consists of majorite + magnesiowüstite with irregular metal-sulfide blebs. The fragments of host chondrites include Ca-rich majorite, hollandite-structured plagioclase, and ringwoodite. Ca-rich majorite ($En_{69}Wo_{22}Fs_9$) occurs in the edge of a 200μm-diameter chondrule in the vein, and consists of a symplectic intergrowth with a Ca-poor amorphous silicate phase. The mineral assemblages of the vein matrix suggest that the crystallization took place between ~ 23 to ~27 GPa, based on the Allende phase diagram (Agee et al 1996). This relatively narrow pressure range suggests that the melt vein crystallized during the equilibrium shock pressure rather than during pressure release. The quench time for this 580 μm wide vein was estimated to be 50 milliseconds, using a finite element heat transfer program to model the thermal quench history of this melt-vein during shock. Because the entire vein contains high-pressure minerals that crystallized from the melt, the shock pressure pulse duration was at least 50 ms. Similarly thermal modeling results for the 1.3-mm wide melt vein in RC106 indicates that crystallized occurred over 225-750 milliseconds. These crystallization times represent minimum shock pulse durations that are much longer than previously estimated durations.

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3. M.S. Theses and Ph.D. Dissertations supported

M.S. Theses

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4. Publications

Journal Articles

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