

Shock effects and argon loss in samples of the Leedey L6 chondrite experimentally shocked to 29–70 GPa pressures

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(Received September 9, 1986; accepted in revised form June 19, 1987)

Abstract—Shock-recovery experiments between 29 and 70 GPa were made on the Leedey L6 chondrite to determine the possible loss of radiogenic Ar caused directly by passage of shock waves, as opposed to purely thermal loss during prolonged post-shock cooling. Experiments were made in vacuum to prevent shock-implantation of terrestrial air, and, following neutron irradiation, the $^{39}\text{Ar}/^{40}\text{Ar}$ ratios were measured by stepwise temperature release. Petrographic examination of experimentally shocked Leedey showed predominantly solid-state effects in the form of increasing disaggregation of component minerals with increasing shock pressure but very little melting, even at the highest shock levels. The melting behavior of the minor feldspar phase was difficult to document, but likely was complete by the higher shock levels. The ^{39}Ar - ^{40}Ar release patterns were complex for both shocked and reference Leedey, probably because of a natural shock history for the meteorite at *ca.* 3.8 Gy. The average ^{39}Ar - ^{40}Ar age for shocked Leedey decreased with increasing shock levels from essentially no change at 29 GPa to a 20% decrease in age at 60 GPa. The feldspar phases degas at lower extraction temperatures and show even greater lowering of ^{39}Ar - ^{40}Ar age with increasing shock pressure. The sample shocked at 69 GPa shows less mechanical disruption than samples shocked to lesser pressures, and also shows a smaller loss of Ar compared to samples shocked at 45 and 60 GPa. We conclude that observed Ar loss is caused by extensive grain fracturing and heating during shock, and that greater Ar loss at low extraction temperatures is enhanced by feldspar melting. None of the experiments duplicated the magnitude of Ar loss commonly seen in naturally shocked materials that lack evidence of pervasive melting. We conclude that large scale gas loss in shocked, but unmelted samples requires that the materials reside for prolonged periods of time at elevated temperatures in a relatively hot impact formation, either inside or outside the crater cavity.

INTRODUCTION

A WIDE VARIETY of shocked samples from the moon, meteorites, and terrestrial impact craters have been studied by the classical K-Ar and the newer $^{39}\text{Ar}/^{40}\text{Ar}$ dating techniques in attempts to determine the time of the impact events (*e.g.*, TURNER, 1969; HARTUNG *et al.*, 1971; WOLFE, 1971; TAYLOR and HEYMANN, 1971; BOGARD *et al.*, 1976; JESSBERGER *et al.*, 1976; SMITH and GOLDSTEIN, 1977; BOGARD and HIRSCH, 1980; WANG *et al.*, 1980; JESSBERGER and OSTERTAG, 1982; STAUDACHER *et al.*, 1982). A few of these studies emphasized the time of Ar loss and broadly assumed this loss to be caused during the passage of a shock wave, thus dating the actual time of crater formation. Others considered it necessary to invoke a prolonged thermal history, *i.e.*, relatively slow cooling rates at elevated temperatures in an ejecta blanket. In many situations complete loss of Ar by either mechanism may still yield geologically meaningful crater ages, because even low cooling rates tend to be short compared to geological time scales. Detailed understanding of the Ar loss mechanism(s) becomes important, however, in the context of partially reset ages, commonly observed in meteorites and lunar rocks. The thermal environment that one may construct from such partially degassed samples depends crucially on the total amount of Ar retained prior to deposition in a "hot" impact formation, and whether shocked rocks have diffusion coefficients similar to those of unshocked materials. As a consequence, direct or indirect effects of shock

compression on the loss of radiogenic Ar are of interest in the dating of impact craters and in understanding the thermal histories of many extraterrestrial samples.

Very few direct studies have been made of the effects of experimental shock on Ar gain and loss in geological materials. FREDRIKSSON *et al.* (1964) artificially shocked fragments and matrix of the Bjurböle chondrite to a pressure of 60 ± 15 GPa (600 Kb) in an Ar atmosphere and measured the Ar released in three stepwise extractions. The purpose of their experiment was to demonstrate that shock could implant significant amounts of a gas into crystal lattices. The amount of atmospheric ^{40}Ar implanted into Bjurböle was very large compared to that in the unshocked sample, 10^{-3} cm³/gram, and was as difficult to degas as was the indigenous Ar. Because the amount of implanted Ar was about 19 times larger than the amount of radiogenic Ar, FREDRIKSSON *et al.* were unable to study the effects of shock on radiogenic Ar.

DAVIS (1977) shocked powder and fragments of a terrestrial basalt to pressures of 6.5, 16, and 27 GPa, neutron-irradiated the samples, and measured the Ar isotopic composition as a function of release temperature. The purpose of Davis' experiment was to determine whether shock could be the cause of the drop in $^{39}\text{Ar}/^{40}\text{Ar}$ ages commonly observed at high extraction temperatures. Although an attempt was made to exclude air-Ar during the shock, atmospheric ^{40}Ar in the samples (0.85 to 98.5×10^{-5} cm³/g) still exceeded the radiogenic Ar for all samples by factors ranging from 1.4 to 118. After correcting for air ^{40}Ar using the mea-

sured ^{36}Ar , the $^{40}\text{Ar}/^{39}\text{Ar}$ release profiles of a basalt (powder shocked to 6.5 GPa and 3 chips shocked to 6.5, 16, and 27 GPa) were essentially identical to those for an unshocked sample. No obvious alteration of the $^{40}\text{Ar}/^{39}\text{Ar}$ plateau due to redistribution of radiogenic ^{40}Ar or K was observed, but the temperature for Ar release was shifted downward by 100–200°C.

Recently, JESSBERGER and OSTERTAG (1982) shocked a terrestrial feldspar (An_{67}) in vacuum, effectively eliminating air-Ar, and quenched it in water. The shock pressures used, 30, 40, and 45 GPa, were purposely intended to evaluate solid state effects. The ^{39}Ar – ^{40}Ar age spectra of these shocked samples were essentially identical with that of an unshocked sample. No obvious Ar loss or redistribution occurred.

CAFFEE *et al.* (1982) measured the effects of experimental shock levels of 7, 20, and 40 GPa on the $^{129}\text{Xe}/^{129}\text{I}$ dating system in the Bjurböle chondrite. They observed disturbance of this isotopic system at all shock levels, and found that the original correlation between iodine and ^{129}Xe was totally destroyed at 20 and 40 GPa. These authors concluded that the observed effects were primarily due to mobilization of iodine by the shock event, and they suggested that the I–Xe system should be more readily disturbed than the K–Ar system.

We decided to expand on these earlier studies and to perform shock recovery experiments, including higher pressures, using the Leedeey L6 chondrite as target material. Initial results were reported by BOGARD *et al.* (1982). We also excluded any prolonged thermal history because the samples cooled within a few minutes to temperatures below 100°C. The experiments were performed in vacuum, eliminating significant interference from atmospheric Ar. Furthermore, a modestly polymict target such as a chondrite differs significantly in its shock behavior from that of single crystal feldspar employed by JESSBERGER and OSTERTAG (1982). In a chondrite specific phases may melt preferentially (*e.g.*, feldspar *versus* pyroxenes), because the deposition of thermal energy is distinctly heterogeneous as described by KIEFFER (1971), AHRENS and COLF (1974), and SCHAAL *et al.* (1979). Highly localized melt zones may be generated at grain boundaries, even at pressures of <30 GPa, and might result in partial degassing of some component minerals without greatly affecting others. Also, at any given stress level, porous targets attain substantially higher bulk temperatures than their dense counterparts. As a consequence the results from dense mono-mineralic targets may not be applied readily to polyphase rocks, particularly to modestly porous, polymict chondrites such as Leedeey.

SAMPLE PREPARATION AND SHOCK EXPERIMENTS

Selection criteria for an ordinary chondrite were that it not have been naturally shocked and degassed of Ar in relatively recent times, and that it be reasonably unweathered. The sample also had to be sufficiently coherent such that the thin sample discs could be prepared. A 15 g piece of the Leedeey L6 chondrite (fell, 1943) was obtained from the Center for Meteorite Studies for the experiment. BOGARD *et al.* (1967)

and HUNEKE *et al.* (1972) had used Leedeey as an Ar standard and found it to contain normal abundances of radiogenic ^{40}Ar ($5.3\text{--}5.6 \times 10^{-5} \text{ cm}^3/\text{g}$). With a K concentration of 0.078%, determined for our unshocked Leedeey sample, these ^{40}Ar concentrations would suggest a K–Ar age for Leedeey of about 4.4 Gy (1 Gy = 1×10^9 years). This age would suggest that Leedeey had not experienced loss of argon due to previous shock events, although many other L6 chondrites are known to have experienced shock and loss of part of their radiogenic argon (*e.g.*, TAYLOR and HEYMANN, 1969). Leedeey, however, had apparently not been studied previously specifically for shock effects. As we shall show, Leedeey does contain effects due to natural shock.

Cylinders ~ 7 mm in diameter were cored from Leedeey and were sliced into wafers ~ 1 mm thick. Plucking of the relatively friable materials during cutting was inhibited by coating the entire core in wax. These raw discs were polished to 0.6 mm thickness and planarity $<1^\circ$ and were cleaned ultrasonically in acetone to remove remnants of the wax and cutting oils (Isomet cutting liquid). The discs were then placed into a dry nitrogen glove box and heated to 105°C for 30 minutes to drive off adsorbed air-Ar. While still in this N₂ environment discs were loaded into target assemblies, which are small, cylindrical sample holders made out of 304 stainless steel (see Fig. 1). Each assembly contains a small target well, custom machined to the exact diameter and thickness of each sample disc. A threaded screw plug was inserted to hold the silicate target firmly in place. The entire target assembly was then temporarily removed from the glove box to be hydraulically pressed into a prepared opening of the target holder, a stainless steel cylinder of $\sim 7 \times 7$ cm dimensions (Fig. 1). The mated pieces were then machined dry in a lathe to assure a flush and planar face to be impacted. This machining lasted 10–15 minutes in terrestrial atmosphere, whereupon the entire assembly was returned to the dry nitrogen box, together with a small, disassembled vacuum chamber.

The target was mounted and pressure-sealed inside this small

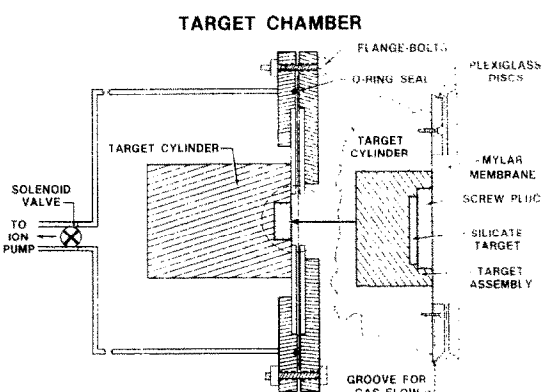


FIG. 1. Schematic configuration of target chamber and sealing mechanisms used to perform shock recovery experiments in the absence of atmospheric Ar. The exploded view at right depicts that the silicate target is press-fit into the target assembly and firmly held by a screw plug; this assembly (20 mm diameter, 7 mm thick) in turn, is press-fit into a much larger metal cylinder (*ca.* 70 \times 70 mm). The primary vacuum seal is provided by a viton O-ring in the chamber flange which holds a 50 μm -thick mylar membrane. This membrane must support substantial differential pressures during the various evacuation and pressurization cycles, and is therefore structurally supported by plexiglass discs. The membrane is free-standing only across a span of 28 mm, which is the projectile's entry hole. The target cylinder is screwed and glued to the inner plexiglass disc; the latter is grooved so as to allow liberal access of gases to the sample area and to permit its efficient evacuation.

vacuum chamber as depicted schematically in Fig. 1, while the complete system was maintained at a slight positive N_2 pressure inside the glove box. The small target chamber was sealed using the solenoid valve and mounted into the much larger impact chamber. Both chambers have independent vacuum pumps and can be flushed or evacuated in an arbitrary sequence. The mylar membrane across the flange of the target chamber maintains the separate vacuum integrity between both chambers until ruptured by the projectile. The following evacuation sequence was used to assure maximum pumping of atmospheric components: The impact chamber was evacuated first to $\sim 10^{-2}$ torr and flushed with a CO/CO_2 (1:1) gas mixture; a second pumping and flushing cycle was made and the facility left overnight at $\sim 10^{-2}$ torr CO/CO_2 . The target chamber was then evacuated to 10^{-5} torr with a diffusion pump, and was next pressurized with CO/CO_2 to >1 atm. Monitoring the vacuum in the surrounding impact chamber assured that the target chamber seals were tight. At that stage the impact chamber was pressurized again with N_2 and opened to insert Polaroid film packages that would fail if left in prolonged vacuum; a generous flow of N_2 was maintained. The chamber was closed, and purged again with CO/CO_2 for ~ 30 min. with the vacuum roughing pump on, and then evacuated to 10^{-2} torr. A second flushing/evacuation cycle was made on both chambers. The final CO/CO_2 pressures prior to launching the projectile were $<10^{-2}$ torr in the impact chamber and $<10^{-6}$ torr in the target chamber.

Actual shock experimentation followed the procedures described previously (HÖRZ, 1970; GIBBONS *et al.*, 1975). The projectile, a cylindrical plastic slug with a metal flyer plate inserted in the front, is launched in a 20 mm gun barrel via conventional explosive powder. He-Ne laser beams and photo diodes are used to measure projectile velocity; X-ray shadow graphs of the projectile in flight are taken to monitor planarity of impact. Experimental shock pressures are deduced from the measured impact velocity according to the graphic impedance match method described by DUVALL and FOWLES (1963) using the equation of state data of MCQUEEN *et al.* (1970) for the various flyer plate metals and the stainless steel target containers. Pressure accuracy is $\pm 3\%$ with a peak pressure pulse-duration of ≤ 1 μ sec. Direct temperature measurements are not possible for these encapsulated silicates, and the temperature estimates given later are those extrapolated from RAIKES and AHRENS (1979).

After projectile impact the powder combustion gases raise the entire shock facility to a pressure of greater than 10^{-1} torr. Terrestrial atmosphere is not allowed to enter the facility for another 15–20 min. The target cylinder, still moderately warm to the touch, is then removed. The impacted face, whatever its state of deformation, is then carefully machined until the silicate wafer is fully exposed. At this state either a petrographic thin section can be made or the material may be plucked and pried loose for gas analysis. Total recovery for the latter purpose is typically 40–80% by weight of the original charge. The remainder of the sample forms an intimate mixture with the highly deformed, metal target container and is not easily recovered.

A total of 17 runs were made at approximately 30, 40, 45, 60, and 70 GPa on both Leedey discs and powders, the latter having a grain size of 125–150 microns and $\sim 40\%$ porosity. Duplicate runs were made at all shock pressures for the disc samples and were used either for Ar analyses or for the preparation of petrographic thin sections (Table 1). Typical sample sizes used for Ar analyses were 45 mg. Because sample recovery was lower for the higher shock pressures, material from two shock runs of essentially identical shock pressure was combined for Ar analysis for the 45 and 70 GPa disc samples and for the 30 and 60 GPa powder samples. Grain mounts were also made of some of the disc material from the 45 and 70 GPa runs that were used for Ar analyses. Thus, petrographic examinations were made both of the same shock runs used for Ar analysis and of separate experiments at essentially identical pressures. Argon analyses were also made on a Leedey

Table 1. Listing of shocked Leedey samples used for petrography (PTS) and Argon (Ar) analyses. The shock level in GPa and the measured concentrations of potassium, calcium, and radiogenic Ar are also given.

SHOCK RUN NO.	SHOCK PRESS. (GPa)	SAMPLE USE	[K] %	[Ca] %	[^{40}Ar] x 10^{-5} cc/g
DISC SAMPLES:					
UNSHK.	0	Ar	0.078	1.00	4.42
745	29.2	Ar	0.061	0.93	3.09
757	30.6	PTS			
746	41.4	Ar	0.060	1.05	2.75
755	40.0	PTS			
749	44.8	Ar	0.044	1.48	2.11
750	45.2	Ar			
758	46.0	PTS			
747	68.7	Ar	0.064	0.74	3.25
748	69.4	Ar			
753	70.5	PTS			
POWDER SAMPLES					
964	29.0	Ar	0.083	1.11	4.51
969	30.2	Ar			
965	59.0	Ar	0.067	0.93	(5.62)
963	60.0	Ar			

disc that underwent the entire sequence of sample processing, but was not shocked, and thus gives an unshocked reference which experienced the same sample treatment.

The shocked Leedey samples were irradiated with fast neutrons in two irradiations, one for the disc samples and one for the powdered samples. The neutron irradiation produces ^{39}Ar from reaction on ^{39}K and ^{37}Ar from reaction on ^{40}Ca . Two samples of a hornblende neutron fluence monitor were included with each irradiation. Each irradiated Leedey sample was heated stepwise in a high vacuum system, and the isotopic abundance of the released Ar was measured on a mass spectrometer. Corrections were made for system blanks, radionuclide decay, and for interfering reactions that also produce Ar. Greater details are given in BOGARD *et al.* (1976).

PETROGRAPHY

Leedey is a typical L6 chondrite (VAN SCHMUS and WOOD, 1967). Its overall texture is that of a recrystallized, clastic deposit (Fig. 2a). Matrix grain size is variable, as is the degree of recrystallization; olivine and pyroxene clasts may be as large as 1 mm. Chondrule relicts are observed only rarely. Feldspar is about 5% of the modal composition, largely confined to the recrystallized matrix or recrystallized, polymict clasts. Fine-grained, transparent masses are interpreted as recrystallized maskelynite. Figure 2a presents an overall view; Fig. 2b is a typical, recrystallized area of Leedey. Note especially in Fig. 2b the relatively unfractured and unstrained nature of the component minerals, predominately olivine in this view. It is important to note that the above textural and grain size heterogeneities are best explained, in our view, by extensive shock-processing of individual clast components prior to breccia compaction, including variable degrees of recrystallization.

The experimentally shocked materials, even those at 70 GPa, display pronounced mechanical effects, but surprisingly little evidence of phase transitions (*i.e.*, melting). Figures 2c and 2d attest to the severe mechanical disruption and disaggregation of all materials

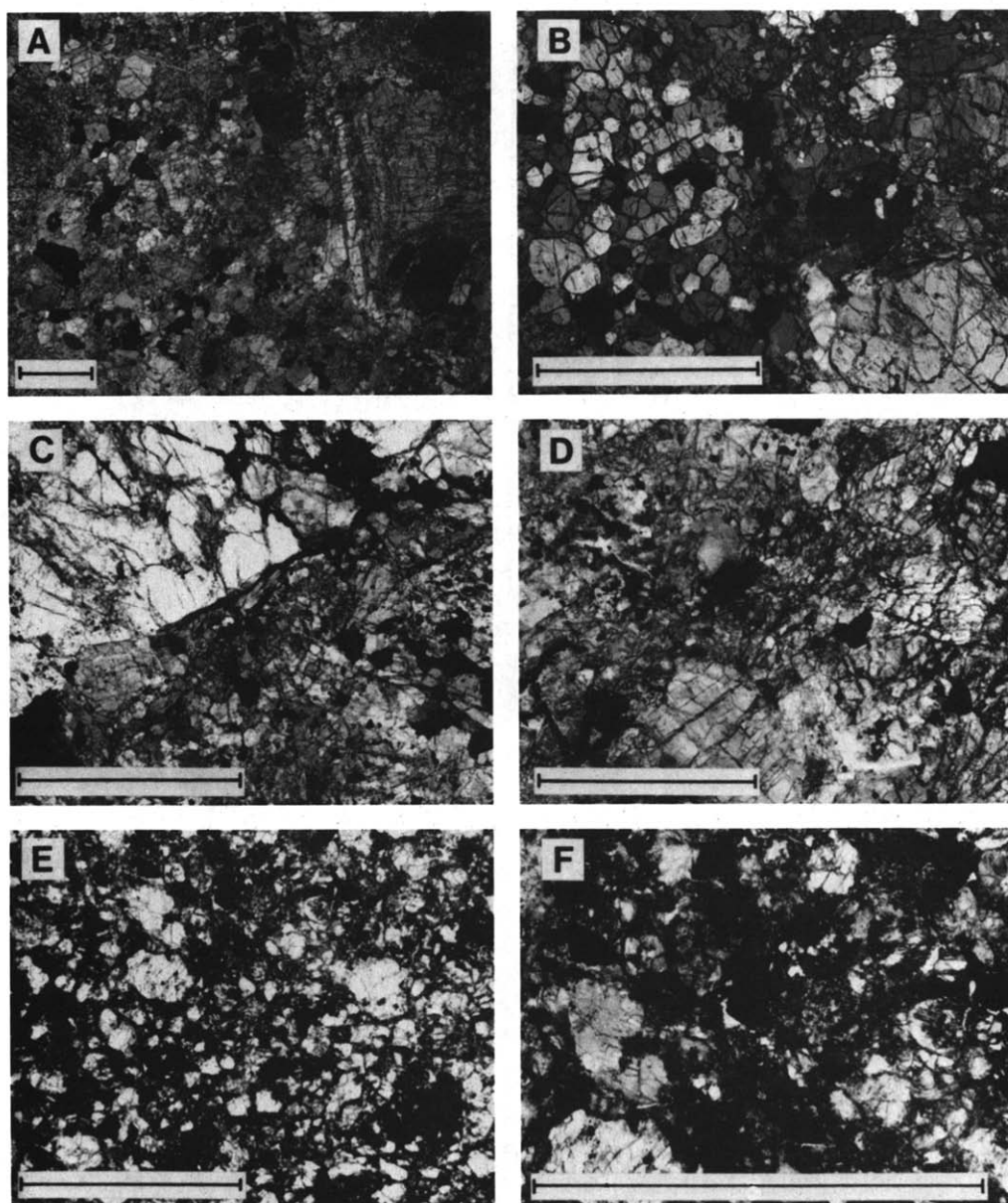


FIG. 2. Photomicrographs of unshocked and experimentally shocked Leedey chondrite taken with partly crossed polarizers. Scale bar is 0.5 mm in all frames. (A) Overall texture of unshocked specimen. Note large, fractured clasts of pyroxene, intermediate-size, lithic clasts recrystallized to various degrees, and fine-grained clastic matrix. A rare chondrule is visible in upper right corner. (B) Detail of unshocked specimen illustrating recrystallized, olivine-rich clast (left half), portion of a large, fractured pyroxene (lower right corner), and fine-grained clastic matrix occurring in pockets and veins. (C) Shocked to 30.6 GPa, note pronounced mechanical disaggregation of Leedey clasts and matrix, including a highly cataclastic, large pyroxene. (D) Shocked to 46.0 GPa: only evidence of increased shock stress is additional fragmentation; commonly brecciation of individual clasts has advanced to a level where it is difficult to determine their initial outlines, in part merging into the (freshly generated) fine-grained, increasingly opaque matrix. Large pyroxene clasts are strongly disaggregated at the peripheries, leading to rounding and overall reduction of clast size. (E) Shocked to 60.0 GPa: compare with (A) and note dramatic decrease in clast size, combined with pronounced rounding and the highly cataclastic nature of most clasts. (F) Shocked to 70.5 GPa: note that many clasts are less comminuted than in the 60 GPa experiment. Nevertheless, pronounced cataclasis is prominent as is the invasion of clasts by very fine-grained matrix. Fine-grained clastic matrix is commonly aligned, attesting to mass movement and mechanical flow, concentrated around clasts.

at 30.6 and 46 GPa, respectively. The pyroxenes and olivines are thoroughly fractured and comminuted, but preserve some degree of coherent extinction on a grain-

by-grain basis. Such pervasive mechanical disruption was described for olivine in shock experiments by REIMOLD and STÖFFLER (1978) and BAUER (1979) for

similar pressures. Again consistent with these observations, especially the high pressure experiments of Bauer, the clasts surviving to shock stresses of 70.6 GPa display distinctly less mechanical disruption (Fig. 2e), although clast size and frequency are decreased. Microscopic disruption of the crystal lattice, however, continues and is evident by irregular, patchy extinction even in grains appearing to be otherwise "homogeneous" in the 70.5 GPa shots. All materials have markedly decreased birefringence. The most diagnostic shock feature is the formation of a fine-grained, opaque matrix as illustrated in Fig. 2e and in enlarged form in Fig. 2f. This material, however, is not molten, but is merely crushed into exceedingly small grains (Fig. 2f). Occasionally, it is "injected" into neighboring cracks that display some lineation resembling flow features.

Because of its low abundance (about 5%), feldspar does not affect the overall texture of the experimental shock products to the degree observed in granitic (STÖFFLER, 1972) or basaltic (SCHAAL and HÖRZ, 1977) lithologies, where the modification and ultimate destruction of the original texture is dominated by tectosilicates. Minor amounts of maskelynite are present in the original Leedeey clasts, and additional maskelynite is generated in the 30 and 46 GPa shocks. Incipient melting of the grain margins was observed in one small area in the 70.6 GPa experiment, but such feldspar melts are exceedingly hard to identify in the fine-grained recovery products. They are expected to be present even at lower pressures, thoroughly mixed with the fine-grained clastic matrix.

In summary, the experimentally shocked Leedeey is almost exclusively characterized by mechanical disaggregation. No pyroxene or olivine melts nor mixtures thereof are observed. The feldspar melts are minor components commensurate with the modal composition of the original starting material.

Ar RESULTS

The measured Ar isotopic data are not given in this paper, but may be obtained from the National Auxiliary Publications Service (NAPS).^{*} The total ^{40}Ar measured for each sample, as well as the calculated K and Ca concentrations, are given in Table 1. Atmospheric Ar was not shock-implanted into most Leedeey samples. The lightly adsorbed, atmospheric argon released in the first two temperature extractions of each sample is typical for crushed silicates; this low-temperature, air-Ar component has a negligible effect on our conclusions, and we ignore it in the following dis-

cussions. Several intermediate temperature extractions released no ^{36}Ar within analytical uncertainties. Most experimentally shocked samples and the reference sample released approximately $0.5 \times 10^{-8} \text{ cm}^3/\text{g}$ of ^{36}Ar , mainly at higher temperatures ($>900^\circ\text{C}$), essentially all of which was produced in Leedeey by cosmic ray interactions in space. The 60 GPa powder sample, however, released appreciable amounts of apparent shock-implanted air-Ar ($^{36}\text{Ar} = 9.9 \times 10^{-8} \text{ cm}^3/\text{g}$), suggesting that we failed to completely exclude air during shock in this experiment. As air ^{40}Ar presumably comprises one-half or more of the total ^{40}Ar measured in this sample, the calculated ages for this sample are meaningless, and its $^{39}\text{Ar}/^{40}\text{Ar}$ release plot is not shown. An isochron plot (also not shown) of $^{40}\text{Ar}/^{36}\text{Ar}$ versus $^{39}\text{Ar}/^{36}\text{Ar}$ for extractions of the 60 GPa powder sample compensates for this air-Ar and indicates a maximum $^{39}\text{Ar}/^{40}\text{Ar}$ age of 3.6 Gy and an average age of 3.15 Gy. Enhanced ^{36}Ar released in the 950°C extraction of the 29 GPa disc sample also suggests a small amount of air-Ar. Because this air component was mainly limited to a single extraction with a relatively small release of ^{39}Ar , it has only a minor effect on the calculated $^{39}\text{Ar}/^{40}\text{Ar}$ age and may make the age high by a few percent.

The $^{39}\text{Ar}/^{40}\text{Ar}$ ages as a function of cumulative release of ^{39}Ar for one unshocked and five shocked Leedeey samples are plotted in Figs. 3 through 6. Releases of ^{39}Ar (produced from K) and ^{37}Ar (produced from Ca) indicate that at least two mineral phases are involved. A phase with essentially constant K/Ca ≈ 0.4 released most of the ^{39}Ar in the temperature region of $500^\circ\text{--}900^\circ\text{C}$, and a phase with K/Ca < 0.01 released less than 15% of the ^{39}Ar at temperatures above 1000°C . The ^{39}Ar released from these two phases is not well resolved, but all six Leedeey samples show es-

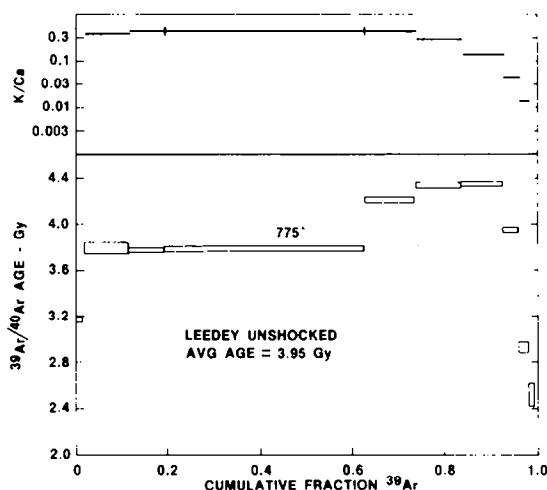


FIG. 3. $^{39}\text{Ar}/^{40}\text{Ar}$ ages as a function of cumulative release fraction of ^{39}Ar for stepwise temperature release of the Leedeey reference sample which was not shocked in the laboratory. Analytical uncertainties in the calculated ages are indicated by the size of the data boxes. The calculated K/Ca ratios as a function of ^{39}Ar release are also given, and are similar for all Leedeey samples.

^{*} See NAPS document No. 04516 for three pages of supplementary material. Order from NAPS c/o Microfiche Publications, P.O. Box 3513, Grand Central Station, New York, NY 10163. Remit in advance in U.S. funds only \$7.75 for photocopies or \$4.00 for microfiche. Outside the U.S. and Canada, add postage of \$4.50 for the first 20 pages, and \$1.00 for each of 10 pages of material thereafter, \$1.50 for microfiche postage.

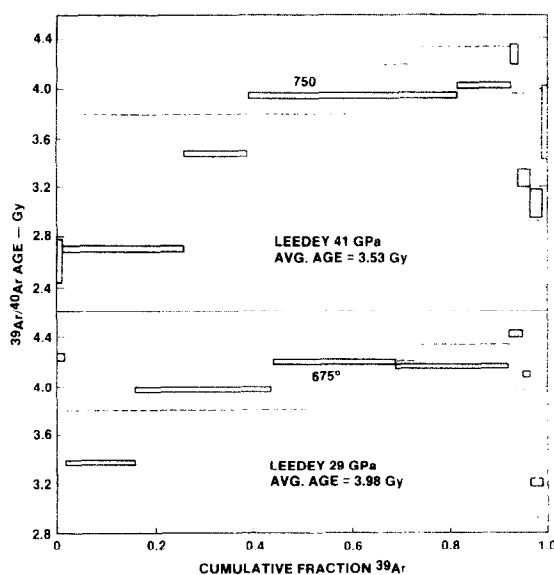


FIG. 4. ^{39}Ar - ^{40}Ar ages as a function of cumulative fraction of ^{39}Ar for stepwise temperature release of Leedeey disc samples shocked to 29 and 41 GPa. The dashed line is the release curve for the unshocked Leedeey sample and is shown for comparison.

essentially the same K/Ca ratio as a function of ^{39}Ar released (e.g., Fig. 3). This behavior of K/Ca ratio as a function of extraction temperature is typical of many

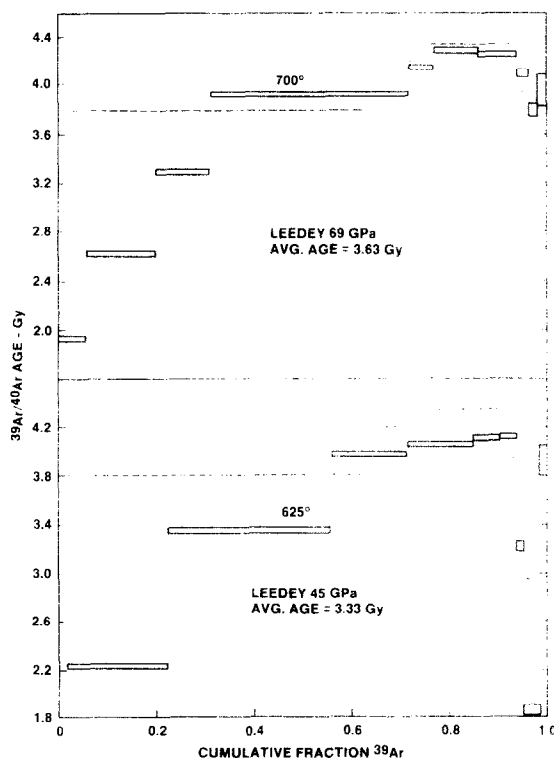


FIG. 5. ^{39}Ar - ^{40}Ar ages as a function of cumulative fraction of ^{39}Ar for stepwise temperature release of Leedeey disc samples shocked to 45 and 69 GPa. The dashed line is the release curve for the unshocked Leedeey sample and is shown for comparison.

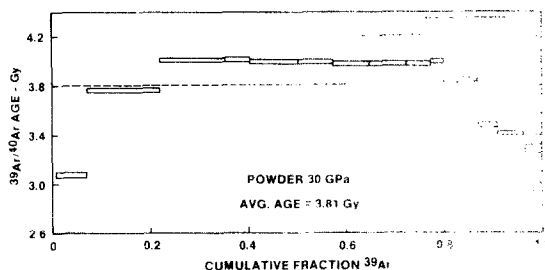


FIG. 6. ^{39}Ar - ^{40}Ar ages as a function of cumulative fraction of ^{39}Ar for stepwise temperature release of Leedeey powder sample shocked to 30 GPa. The dashed line is the release curve for the unshocked Leedeey sample and is shown for comparison.

chondrites, and is consistent with the lower temperature phase being feldspar and the higher temperature phase being pyroxene (e.g., BOGARD *et al.*, 1976; WANG *et al.*, 1980; BOGARD and HIRSCH, 1980). The drop in ^{39}Ar - ^{40}Ar ages shown by all Leedeey samples in the last $\sim 5\%$ of their ^{39}Ar release is interpreted as an effect caused by reactor-induced recoil of ^{39}Ar into the K-poor pyroxene (TURNER and CADOGAN, 1974; HUNEKE and SMITH, 1976). This recoil effect was more extensive in the 30 GPa powder sample, presumably because of the crushing and mixing of mineral grains prior to experimental shock.

The feldspar phase of the reference Leedeey sample has been partially reset to an apparent ^{39}Ar - ^{40}Ar plateau age of 3.8 Gy from an age of ≥ 4.4 Gy. Although some loss of ^{40}Ar might have occurred during sample heating in the extensive sample preparation stage, the presence of obvious natural shock features in Leedeey suggests that the ^{40}Ar loss occurred during a shock-heating event ~ 3.8 Gy ago which degassed $\sim 75\%$ of the ^{40}Ar in the meteorite at that time. The averaged ^{39}Ar - ^{40}Ar age of the reference Leedeey sample is 3.95 Gy. Loss of ^{40}Ar in Leedeey due to natural shock was unexpected, as it was not observed in previous analyses of Leedeey, and complicates our goal of examining loss or redistribution of Ar as a function of shock pressure. Significant Ar loss in these samples would still be obvious, but to detect small Ar losses or Ar redistribution, we rely on the averaged ^{39}Ar - ^{40}Ar ages and details of the release profiles.

The six experimentally shocked Leedeey samples give evidence of decreasing ^{39}Ar - ^{40}Ar ages, and thus increasing loss of ^{40}Ar , with increasing shock pressure (Table 2). For the same or similar shock pressures, there is some tendency for powder samples to show greater Ar loss than disk samples. Compared to the average ^{39}Ar - ^{40}Ar age of the Leedeey reference sample, this ^{40}Ar loss ranges from zero at 29 GPa to about 32% for the disc shocked to 45 GPa and about 39% for the powder shocked to 60 GPa. Argon is also more easily degassed in the laboratory from shocked samples compared to the unshocked sample, presumably as a result of the observed decrease in mean grain size. For example, the temperatures by which 50% and 90% of the ^{39}Ar has been degassed average about 100°C and 150°C

Table 2. Average ^{39}Ar - ^{40}Ar ages and ages at 5 percent of ^{39}Ar release for six shocked and one unshocked sample of the Leedey chondrite.

SHOCK, GPa & SAMPLE TYPE*	^{39}Ar - ^{40}Ar AGE, Gy		PETROLOGICAL CHARACTERISTICS
	AVG.	5% ^{39}Ar	
0 -D	3.95	3.8	Modest fracturing & strain in clasts & matrix; highly recrystallized
30 -D	3.98	3.4	Pronounced fracturing of mafics; matrix disaggregation; rare maskelynite
40 -D	3.53	2.7	Severe fracturing; increased disaggregation of clasts and matrix
45 -D	3.33	2.2	Severe fracturing and disaggregation; pockets of pervasive, fine-grained, opaque matrix
70 -D	3.65	1.9	Remaining clasts less fractured; fine-grained, clastic matrix increased into large contiguous areas; rare, transparent melts of feldspar
30 -P	3.81	3.1	**
60 -P	3.15	2.8	**

* D-disk sample; P-powder

** No petrographic thin sections were prepared for powdered samples. The findings of Schaaf et al. (1979) and Bauer (1979) indicate the possibility that some melting of pyroxene and olivine occurred, especially in the 60 GPa experiment.

lower, respectively, for the shocked samples compared to the unshocked sample. This difference was also observed by DAVIS (1977) for terrestrial basalt shocked to lower pressures. Just the opposite trend was noted for several severely shock-heated chondrites, where Ar was overall more difficult to degas (BOGARD and HIRSCH, 1980).

Compared to the reference sample, all shocked samples show even greater decreases in $^{39}\text{Ar}/^{40}\text{Ar}$ age at low extraction temperatures than they do for average ages. This tendency for greater loss of low-temperature Ar with increasing shock levels is most apparent in the ^{39}Ar - ^{40}Ar age at ~ 0.05 fractional release of ^{39}Ar (Table 2), and can also be seen by comparing Figs. 4 and 5. This trend indicates that shock has degassed Ar more efficiently from the lower-temperature feldspar phase than from the higher-temperature phase. The trend is consistent with the petrographic observations that feldspar was melted by shock levels about 40–45 GPa, whereas mafic minerals did not experience melting at any shock level (Table 2). On the other hand, disk samples shocked to 41 and 45 GPa and the powder sample shocked to 30 GPa also show significantly lower ages in their high temperature phase compared to unshocked Leedey, which suggests Ar loss from the high temperature phase by processes related to grain fracturing rather than feldspar melting.

The 70 GPa sample shows a higher averaged age than the trend between age and shock level would predict. A maximum correction made by (falsely) assuming that all ^{36}Ar (including cosmogenic Ar) was atmospheric would lower the age to only 3.35 Gy. The 70 GPa sample shows distinctly less mechanical disruption of the preserved clasts than the 45 GPa sample.

Such a decrease in mechanical disruption was also described from shock recovery experiments on olivine by BAUER (1979). Less disruption would tend to enhance Ar retention in the high-temperature phase, and is perhaps the explanation for the higher ^{39}Ar - ^{40}Ar ages for the most retentive phases of the 70 GPa sample. Thus, in spite of the higher shock intensity experienced by the 70 GPa sample and the greater ^{40}Ar loss from low retention sites, the degree of mechanical disruption and the overall ^{40}Ar loss is less than those in disc samples experiencing lesser shock levels. This observation suggests that experimental shock pressures higher than 70 GPa under these experimental conditions would not cause greater ^{40}Ar loss.

Not all of the differences among the ^{39}Ar - ^{40}Ar profiles of Figs. 3–6 are readily explained by Ar loss, but may in part represent redistribution of some ^{40}Ar during shock. Differences in relative abundances of mineral phases may also be a factor, as large, individual clasts may constitute a substantial fraction of the small target discs. It is conceivable that a small amount of the ^{40}Ar in K-rich phases such as feldspar could be shock-implanted into K-poorer phases, thereby changing the shape of the ^{39}Ar - ^{40}Ar release profile. This explanation may account for the tendency in shocked samples for the ages at intermediate extraction temperatures to exceed the 3.8 Gy age plateau in unshocked Leedey. The 30 GPa powder sample, where 8 temperature steps released 58% of the ^{39}Ar and showed a plateau "age" of 4.0 Gy, gives the best example of possible shock redistribution of Ar among the crushed, mixed grains.

In a study of the naturally shocked Peace River chondrite, McCONVILLE *et al.* (1985) noted that a shock-melted glass vein was depleted in K by a factor

of two or more relative to the bulk meteorite. This observation raised the question of whether shock could also cause loss or redistribution of K. The K and Ca concentrations calculated for our Leedeey samples (Table 1) do not suggest a systematic trend of K loss with increasing shock pressure. The observed variations in K and Ca concentrations among most samples is perhaps an expected consequence of heterogeneity among our small sample sizes and of analytical uncertainties in concentrations (estimated at 10–15%). The much lower K concentration of the 45 GPa disc sample (which showed the greatest textural effects of shock) may represent some K loss; however, the higher Ca concentration of this sample also suggests a different proportion of K and Ca-bearing minerals in this sample compared to the others. Alternatively, the low shock recovery yield for this sample may have caused some selective loss of K in sample recovery. We also did not note any significant difference in ^{39}Ar release as a function of temperature between shocked and unshocked disk samples, except for the small decrease in average release temperature noted above for ^{40}Ar . This suggests that shock redistribution of K among phases was minor.

CONCLUSIONS

Petrographic observations on thin-sections fabricated from solid discs indicate that the dominant shock effects are mechanical disaggregation and increasing cataclasis, both solid state effects. Pyroxene and olivine are the dominant phases, and they did not melt at <70 GPa. Feldspar observable in the unshocked meteorite is rather rapidly obstructed and essentially not traceable in the shock products *via* optical examination. The few observations that can be made are consistent with the general behavior of feldspar under shock (*e.g.*, STÖFFLER, 1972), and thus, it is assumed that Leedeey feldspars transformed to maskelynite at approximately 30 GPa and to melt at approximately 50 GPa.

None of the experimentally shocked samples of Leedeey, a typical L6 chondrite, was strongly degassed of radiogenic Ar. Intense shock as high as 70 GPa, substantially higher than employed in previous shock experiments, apparently does not cause appreciable gas loss either from solid discs or from relatively fine-grained powder. All shocked samples, however, except the 29 GPa disc sample, appear to have lost modest amounts of Ar, with greater loss associated with higher shock levels. Detailed examination suggests that this Ar loss was the result of mechanical disruption of grains, and was enhanced by partial melting of feldspar, which degasses at low temperatures. Average temperatures for the 70 GPa experiment immediately after the shock event are estimated as <800°C based on work by RAIKES and AHRENS (1979) and BAUER (1979), but local temperatures could be substantially higher, possibly exceeding the melting temperature of all mineral phases. Modest melting, predominantly at grain boundaries and especially in feldspar, cannot be

excluded, despite the seemingly negative evidence from the microscope.

The observation made here that the 29 GPa sample did not lose noticeable amounts of ^{40}Ar is consistent with the results of DAVIS (1977), in which terrestrial basalts shocked to 6.5, 16, and 27 GPa also did not lose ^{40}Ar . JESSBERGER and OSTERTAG (1982), however, did not see noticeable Ar loss in samples of a single, terrestrial labradorite crystal (An_{67}) shocked to 30, 40, and 45 GPa. These samples were quenched in water seconds after being shocked, raising the question of whether Ar loss in our Leedeey samples (which cooled in vacuum) occurred in an extended, hot environment after shock. Our experience based on many shock experiments is that the large (~ 1 kg) metal container around the sample during shock reaches an equilibrium temperature of no more than 100°C within a few minutes after shock. This time-temperature environment is insufficient to cause the observed Ar loss. For example, from the stepwise temperature data of the 69 GPa sample, we calculated the diffusion parameter D/a^2 (FECHTIG and KALBITZER, 1966) for Ar in the lower-temperature phase, which is richer in K, and examined these in an Arrhenius plot. Although these data are not particularly "well-behaved", they do give an estimate of the Ar diffusion characteristics in this shocked sample and show them to be slightly higher than unshocked Leedeey. From these approximate D/a^2 data and models of thermal cooling and gas diffusion (*e.g.*, BOGARD and HIRSCH, 1980), we estimate that to lose 10% of the ^{40}Ar from the lower temperature phase at a temperature of 200°C would require a very long time, on the order of a year. Even at 800°C, minutes would be required to produce significant Ar loss from shocked Leedeey. We conclude that it is most unlikely that the observed ^{40}Ar loss even in strongly shocked Leedeey samples occurred while the metal sample holder cooled inside the shock chamber.

The Leedeey disc samples shocked to 40–45 GPa lost ~ 20 –30% of their ^{40}Ar , whereas single crystal anorthites shocked to similar pressure by JESSBERGER and OSTERTAG (1982) experienced no observable Ar loss. Labradorite shows a considerably greater resistance to Ar diffusion than Leedeey, due in part to the greater diffusion distance required in the single crystal before the diffusing Ar reaches a grain surface with low activation energy. An Arrhenius plot of D/a^2 for Ar diffusion in the 45 GPa anorthite sample of Jessberger and Ostertag suggests that Ar diffusion at 800°C was about two orders of magnitude slower in the shocked anorthite compared to shocked Leedeey. The differences in Ar loss observed between single crystal feldspar and Leedeey may also be due to relative differences in energy deposition between the single-crystal target and the heterogeneous and modestly porous chondritic breccia. Heterogeneity in phases causes shock reverberations and heterogeneous deposition of energy, particularly if combined with free surfaces in a porous target (KIEFFER, 1971; AHRENS and COLE, 1974). Thus pressure and temperature may vary locally on much larger

scales in the breccia than they do in single crystals at the same average shock level. Also the average temperature at any given shock level is higher in porous media compared to their dense counterparts, and Leedey samples, on average, experienced higher temperatures than the labradorites. SIMON *et al.* (1985) also demonstrated that fine-grained target components melt much more readily than coarse materials. This effect is supported by the observations that Ar loss was greater in powder samples compared to disc samples and that overall Ar loss did not increase significantly in those Leedey disc samples shocked above 45 GPa, *i.e.*, above pressures where all feldspar is probably molten at temperatures of 1100–1200°C.

In summary, loss of radiogenic Ar during the direct passage of a shock wave depends upon the shock pressure reached and the sample porosity, but probably ranges from no loss to modest loss for most non-porous materials. Whereas previous studies found no Ar loss, the Leedey data reported here examines higher shock levels with finer-grained, more porous materials, specifically polymict chondritic meteorites. The Ar loss and redistribution in shocked Leedey samples was probably caused by a combination of mechanical grain disruption and feldspar melting. Some redistribution of ^{40}Ar among mineral phases may have occurred also. Both processes tend to increase in magnitude with increasing shock level, except that mechanical disruption may decrease again in solid samples at very high shock levels. K loss or redistribution appear not to have occurred. None of the strongly shocked Leedey samples likely experienced bulk temperatures above 800°C, but feldspars in the most strongly shocked samples probably reached their melting point.

The conclusions given here strictly apply to Ar loss caused by the shock process itself, and not to Ar loss caused by a long-lasting thermal environment possibly produced by natural shock processes. Argon loss observed in many naturally shocked materials, especially those that lack pervasive evidence of melting, probably occurred while the specimen was exposed to elevated temperatures for considerable time periods as part of a relatively hot impact formation, either outside or inside the crater cavity.

Acknowledgements—We thank Carleton Moore for supplying the sample of Leedey, R. Schmidt for assistance in the shock experiments, and Robert Spangler for assistance in part of the gas analyses. Constructive comments by Grenville Turner and an anonymous reviewer improved the manuscript.

Editorial handling: F. A. Podosek

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