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 ^{39}Ar - ^{40}Ar evidence for early impact events on the LL parent bodyE. T. DIXON,^{1,*} D. D. BOGARD,¹ D. H. GARRISON,¹ and A. E. RUBIN²¹ARES, code SR, NASA Johnson Space Center, Houston, TX 77058, USA²Institute of Geophysics and Planetary Physics, University of California Los Angeles, Los Angeles, CA 90095-1567, USA

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Abstract—We determined ^{39}Ar - ^{40}Ar ages of eight LL chondrites, and one igneous inclusion from an LL chondrite, with the object of understanding the thermal history of the LL-chondrite parent body. The meteorites in this study have a range of petrographic types from LL3.3 to LL6, and shock stages from S1 to S4. These meteorites reveal a range of K-Ar ages from ≥ 3.66 to ≥ 4.50 Ga, and peak ages from ≥ 3.74 to ≥ 4.55 Ga. Significantly, three of the eight chondrites (LL4, 5, 6) have K-Ar ages of ~ 4.27 Ga. One of these (MIL99301) preserves an ^{39}Ar - ^{40}Ar age of 4.23 ± 0.03 Ga from low-temperature extractions, and an older age of 4.52 ± 0.08 Ga from the highest temperature extractions. In addition, an igneous-textured impact melt DOM85505,22 has a peak ^{39}Ar - ^{40}Ar age of ≥ 4.27 Ga.

We interpret these results as evidence for impact events that occurred at about 4.27 Ga on the LL parent body that produced local impact melts, reset the ^{39}Ar - ^{40}Ar ages of some meteorites, and exhumed (or interred) others, resulting in a range of cooling ages. The somewhat younger peak age of 3.74 Ga from GRO95658 (LL3.3) suggests an additional impact event close to timing of impact-reset ages of some other ordinary chondrites between 3.6–3.8 Ga. The results from MIL99301 suggest that some apparently unshocked (S1) chondrites may have substantially reset ^{39}Ar - ^{40}Ar ages. A previous petrographic investigation of MIL99301 suggested that reheating to temperatures less than or equal to type 4 petrographic conditions (600°C) caused fractures in olivine to anneal, resulting in a low apparent shock stage of S1 (unshocked). The ^{39}Ar - ^{40}Ar age spectrum of MIL99301 is consistent with this interpretation. Older ages from high-T extractions may date an earlier impact event at 4.52 ± 0.08 Ga, whereas younger ages from lower-T extractions date a later impact event at 4.23 ± 0.03 Ga that may have caused annealing of feldspar and olivine. Copyright © 2004 Elsevier Ltd

1. INTRODUCTION

There are important unanswered questions concerning the thermal history of the LL parent body. For example, do the LL chondrites show a larger range in ^{39}Ar - ^{40}Ar cooling ages than do the H-chondrites, as might be expected if the LL asteroidal parent body was larger than the H-parent body (e.g., Lipschutz et al., 1989; Pellas and Fieni, 1988)? If true, LL chondrites could show a larger range in ^{39}Ar - ^{40}Ar cooling ages than H chondrites. However, there have been relatively few investigations into the relationship between petrography and chronology of LL chondrites that would provide insights into this question (Hohenberg et al., 1981; Kaneoka, 1980; Kaneoka, 1981; Pellas et al., 1990; Trieloff et al., 1989; Turner and Cadogan, 1973), in contrast to the more numerous studies of H and L chondrites and their parent-body structures (Anders, 1978; Bogard, 1995; Dodd, 1969; Grimm, 1985; Keil et al., 1994; Lipschutz et al., 1989; Minster and Allegre, 1979; Pellas, 1982; Pellas and Fieni, 1988; Pellas et al., 1990; Pellas and Storzer, 1981; Scott, 2003; Scott and Rajan, 1979; Scott and Rajan, 1981; Taylor et al., 1987; Trieloff et al., 2003). Relating existing ^{39}Ar - ^{40}Ar cooling ages to original parent body structure would also require understanding of whether there has been extensive impact-resetting on the parent body. Most LLs do not show

evidence for extensive resetting by late impacts (Lipschutz et al., 1989; Pellas and Fieni, 1988), but it is not known whether heat from early impacts has extended the duration of early metamorphism.

The possible extent of early impact-resetting on the LL-parent body also cannot be properly evaluated from the few ^{39}Ar - ^{40}Ar data that exist for LL chondrites because either the shock grade is not provided, there are insufficient data for a given petrographic type, or the age spectra are highly disturbed. The existing dataset includes dates for one LL3 chondrite (4.50 ± 0.05 Ga; Kaneoka, 1980) and 10 LL5-7 chondrites (3.9 Ga to 4.42 ± 0.03 Ga), including four analyses of St. Severin (Hohenberg et al., 1981; Kaneoka, 1981; Pellas et al., 1990; Trieloff et al., 1989; Trieloff et al., 1994; Turner and Cadogan, 1973; Turner et al., 1978). Other results from LL5-6 chondrites with highly disturbed argon spectra have relatively old minimum ages of 4.18 to 4.51 Ga (Bernatowicz et al., 1988). This total range of ages, from ~ 3.9 Ga to 4.55 Ga, or 0.65 Ga, is much larger than the 0.08 ± 0.02 Ga range for apparently unshocked H chondrites. However, we do not know the shock history of most of these LL chondrites, and further investigation is needed to understand the thermal history of the LL chondrite parent body.

In this study, ^{39}Ar - ^{40}Ar chronology of eight LL chondrites and one igneous impact melt fragment are used to help evaluate the thermal history of the LL-parent body. Because impacts can cause partial- to complete resetting of the ^{39}Ar - ^{40}Ar age, we evaluate the possible relationships between different shock stages and the extent of resetting of the ^{39}Ar - ^{40}Ar age. Com-

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Table 1. Petrographic type, shock and weathering grades.

Meteorite	Type	Shock	Weathering
MIL99301	LL6	S1	W1
PCA91416	LL6	S4	W1
QUE97028	LL5	S3	W1
QUE97071	LL5	S2	W1
DOM85505,23	LL5	S3	W2
DOM85505,22	igneous	*	W2
GRO95552	LL4	S3	W3
Savtschenskoje	LL4	S2	W0
GRO95658	LL3.3	S2	W2

* Not appreciably shocked after melting.

bined with the ^{39}Ar - ^{40}Ar results from previous studies, we use our results to evaluate the cooling and impact history of the LL chondrite parent body.

2. SAMPLES AND PROCEDURES

We focus our investigation on meteorites that have a range of petrographic types from LL3.3 to LL6, and shock stages of S1 to S4 (Stoffler et al., 1991) that include: Grosvenor Mountains (GRO) 95658 (LL3.3); Savtschenskoje (LL4); GRO95552 (LL4); Dominion Range (DOM) 85505,22 (LL5 igneous impact melt fragment); DOM85505,23 (LL5 chondrite); Queen Alexandria Range (QUE) 97071 (LL5); QUE97028 (LL5); Pescora Escarpment (PCA) 91416 (LL6); and Miller Range (MIL) 99301 (LL6) (Table 1). Most of these meteorites are relatively unweathered (W0–W2), with the exception of GRO95552, which has a weathering grade of W3 (Table 1). DOM85505,22 is an impact melt fragment from host DOM85505,23. Significantly, Miller Range 99301 (MIL99301) is an unbrecciated LL6 chondrite that has a low shock stage of S1 despite containing evidence for previous shock events (Rubin, 2002). The olivine and plagioclase in MIL99301 were interpreted to have been shocked and subsequently annealed (Rubin, 2002). The high Ni content in taenite, usually an indicator of slow cooling, may have resulted from equilibration during the postshock annealing phase experienced by the meteorite. If the plagioclase grains have been annealed to an apparent shock grade of S1 under type-4 metamorphic conditions by heat produced during impact events (Rubin, 2002), then we expect the ^{39}Ar - ^{40}Ar age of the feldspar to have been reset to the time of impact.

The experimental methods and data reduction procedure used in this study are identical to those reported in Dixon et al. (2003), and described previously by Bogard and Hirsch (1980) and Bogard et al. (2000), except that the LL-chondrites were not acid-etched before irradiation.

3. RESULTS

3.1. Interpretation of Complex Ar-Ar Age Spectra

All Ar-Ar age spectra obtained are complex and require varying degrees of interpretation. Some of this interpretation is based on characteristics of Ar isotopic data for meteorites that we believe to be well understood, whereas other interpretations are more subjective in nature. In this section we summarize some of the general characteristics of the Ar data and its use in deriving an Ar-Ar age.

For all of the chondrites in this study, argon isotopes are released from more than one diffusion domain. These diffusion domains may represent different minerals, different crystal sizes (or diffusion paths) of a common mineral, or terrestrial weathering products that coat mineral grains. Different Ar diffusion domains for chondrites are well known from previous studies (e.g., Bogard and Hirsch, 1980; Bogard et al., 1976; Turner et al., 1978). Different diffusion domains of Ar can be indicated in the stepwise temperature release data by distinct peaks in the rate of release of ^{39}Ar and ^{37}Ar , by changes in the K/Ca ratio, or by significant differences in Ar diffusion properties when the ^{39}Ar data are used to construct an Arrhenius plot. In addition, changes in the $^{37}\text{Ar}/^{36}\text{Ar}$ ratio with extraction temperature can indicate release of terrestrial Ar from weathering products at low temperatures or trapped meteoritic argon at higher temperatures. Argon-37 is produced entirely in the nuclear reactor from Ca and resides in the same lattice sites as cosmogenic ^{36}Ar . Thus, the addition of trapped ^{36}Ar results in a higher $^{36}\text{Ar}/^{37}\text{Ar}$ ratio. The use of the Ar isotopic composition to identify these different components has been extensively discussed (Garrison et al., 2000).

A second type of complication in interpreting these Ar-Ar age spectra is that most show substantial evidence of recoil redistribution of ^{39}Ar that occurred during its production by neutron-capture in the reactor (Huenke and Smith, 1976; Turner and Cadogan, 1974). Several spectra show relatively young ages (≤ 2.5 Ga) associated with relatively low K/Ca phases (e.g., pyroxene) in the highest temperature gas extractions, and some show very old ages (≥ 4.55 Ga) associated with relatively high K/Ca phases (e.g., feldspar) in the low-temperature extractions. The sites depleted in ^{39}Ar typically degas at low temperatures, whereas the sites enriched in ^{39}Ar degas at relatively high temperatures. These kinds of disturbed spectra are common in chondrites with relatively fine-grained mineral textures, and the existence of potassium in more than one diffusion domain has caused these recoil effects to be more pronounced than in some other chondrite classes. Recoiled ^{39}Ar also obscures much of the evidence for possible recent diffusive loss of ^{40}Ar that is commonly observed in low-temperature extractions. However, the possible extent of diffusive loss of ^{40}Ar needs to be determined to understand whether the maximum observed ^{39}Ar - ^{40}Ar age from high-temperature extractions (t_{peak}) are minimum estimates of the age, as in the case of pervasive ^{40}Ar loss, or alternatively good estimates of the age, if ^{40}Ar loss was minimal.

The method we used to evaluate the possible extent of diffusive ^{40}Ar loss corrects the ^{39}Ar release spectrum for the effects of recoiled ^{39}Ar . In general, this is accomplished by modeling the redistribution of excess ^{39}Ar from the high-temperature extractions to the low-temperature extractions (Dixon et al., 2003; Turner et al., 1978). Initially, we subtract atmospheric argon from the low-temperature extractions, using changes in the $^{36}\text{Ar}/^{37}\text{Ar}$ and $^{36}\text{Ar}/^{38}\text{Ar}$ ratios as a function of temperature as a means by which to evaluate the amount of atmospheric argon in each extraction (Garrison et al., 2000). Secondly, the young ages from the highest temperature extractions are corrected for gain of recoiled ^{39}Ar by subtracting ^{39}Ar until they form a plateau with an age equal to the peak age observed at intermediate temperatures (any deviations from this approach will be justified below). The total amount of ^{39}Ar

subtracted from high-T sites is then redistributed into the low-T extractions so as to decrease the oldest ages. The aim of the ^{39}Ar redistribution is to determine whether the age spectrum could have been consistent with a typical diffusive loss profile. Finally, we evaluate the shape of the resulting Ar-Ar age spectrum to assess whether it can be reconciled with diffusive loss of ^{40}Ar , or if other more complex processes must be invoked. In this assessment we generally assume that recoil redistribution of ^{39}Ar does not affect the Ar released from the interiors of feldspar grains just before Ar release from pyroxene (where the K/Ca ratio shows a substantial decrease). Although this assumption seems to be valid for most meteorites, it may not be true for meteorites whose K-bearing phases are very fine-grained, as is apparently the case for low-metamorphic-grade chondrites, or for meteorites where the age spectrum has been strongly disturbed by shock or weathering. Thus, in addition to the determined Ar-Ar age profile for each meteorite, we also show this “corrected” Ar-Ar age spectrum. We emphasize that these corrected age spectra are artificial constructs generated in a consistent manner for each meteorite (unless otherwise stated) by making some reasonable assumptions about the nature of the ^{39}Ar recoil redistribution. However, they are useful in evaluating the extent of recent diffusion loss of ^{40}Ar , and thus in deriving the preferred Ar-Ar age interpretation.

We outline below several case situations that may occur for a given meteorite, depending on its grain-size, the number of K-bearing phases that are present, and its thermal history. Here we define the “peak” age as the maximum age observed in the intermediate- or high-temperature portion of the age spectrum. Our age spectra do not typically form what is conventionally termed a “plateau,” which by one definition, should consist of high-temperature extractions that comprise more than 50% of the ^{39}Ar released and have the same age within uncertainty (McDougall and Harrison, 1999). In the case of the LL-chondrites, where the age spectra are very complex, it is necessary to understand and interpret the entire age spectrum to interpret the validity of the ages. Consequently, we here define the term “pseudo-plateau” to describe the situation where two or more gas extractions, from intermediate or high temperature, have the same age.

3.2. Case 1

The Ar age spectrum, corrected for ^{39}Ar recoil redistribution, is flat across most extractions and indicates no ^{39}Ar recoil loss and little to no ^{40}Ar diffusion loss. In this case, the total summed age is probably valid. If an Ar-Ar quasi-plateau exists at intermediate temperature, we would expect it to be similar to the total age (Turner et al., 1978).

3.3. Case 2

After correction for redistributed recoiled ^{39}Ar , the ages at low-T are younger than the ages at mid-T and high-T, which indicates that some diffusion loss of ^{40}Ar has occurred. In this case we expect the total age to be younger than any quasi-plateau at intermediate temperatures. If the intermediate age plateau is well-developed, we would expect it to be valid. If

not, we would expect it to give a lower limit to the time of last major ^{40}Ar degassing.

3.4. Case 3

After correction for ^{39}Ar redistribution, the ages at low T are older than the ages at high T. This could indicate some loss of ^{39}Ar from the sample, where not all ^{39}Ar that originated from low-T, high-K phases was added to high-T, low-K phases (see also Case 6). In this case, if the amount of ^{40}Ar loss is minimal, we would expect the total age to exceed any plateau age. Otherwise, in the case of extensive diffusive ^{40}Ar loss, recoiled ^{39}Ar loss may not result in peak ages in excess of the total gas age (see Case 4). In either case, only the plateau age or pseudoplateau age could give a valid age.

3.5. Case 4

Some meteorites may have lost both ^{39}Ar and ^{40}Ar from low-T sites. If these losses are comparable for the two isotopes, their loss may not be apparent. Again, only the plateau age could give a valid age.

3.6. Case 5

In the LL data reported here, there is one sample where loss of recoiled ^{39}Ar has affected almost the entire age spectrum and which consequently shows unrealistically old ages even at intermediate temperatures, where we normally expect degassing only from the interior of K-bearing phases. This type of behavior is not expected in coarse-grained, equilibrated meteorites, because recoiled ^{39}Ar is expected to be lost only from fine-grained K-rich phases, or the exterior of coarser-grained K-rich phases in low-temperature extractions. Such behavior is more likely in unequilibrated, fine-grained meteorites. In this case the total age is the only one that can be derived, and it may or may not give a valid age.

3.7. Case 6

There is also at least one LL chondrite in which both the K-poor phase (e.g., pyroxene) and the K-rich phase (i.e., feldspar) appear to degas at intermediate temperatures. This is suggested by a stepwise decrease in the K/Ca ratio throughout the age spectrum, as opposed to what is observed from the majority of meteorites in this study, where the K/Ca ratios are relatively constant from low to intermediate temperature, then decrease sharply to very low ratios at the onset of major pyroxene degassing. The stepwise decrease in the K/Ca ratio over the entire age spectrum suggests recoiled ^{39}Ar may be degassed from the exterior of pyroxene grains over a very broad range of temperatures. In this case, the “peak” age from intermediate temperature is a minimum estimate. Consequently, the amount of recoiled ^{39}Ar , as determined from the reconstructed age spectrum, would be underestimated, because it is based on the difference between the relatively young ages from high-temperature extractions and the peak age at intermediate temperature. The corrected age spectra in such meteorites are likely to have relatively old ages from low-temperature extractions, but the total gas age may give a valid age.

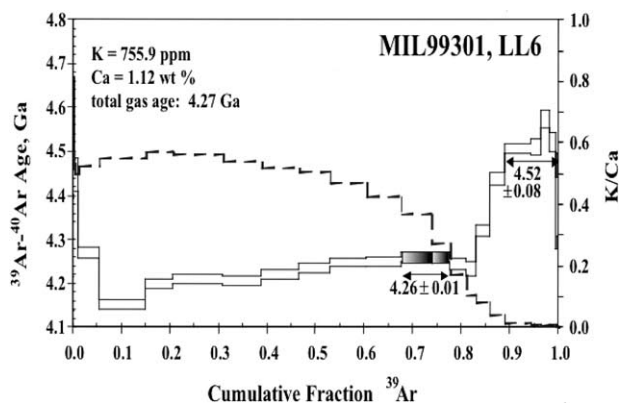


Fig. 1. Plot of ^{39}Ar - ^{40}Ar ages (rectangles, primary y-axis) and K/Ca ratios (dashed line, secondary y-axis) as a function of cumulative release of ^{39}Ar for stepwise temperature extractions of LL6 chondrite, MIL99301. The decrease in the K/Ca ratio from high values at low T to very low values at high T shows this sample is a mixture of two K-bearing "phases" that have different Ar release properties and very different ^{39}Ar - ^{40}Ar ages. The age of the older phase is 4.52 ± 0.08 Ga. The age of the younger phase, from summed extractions between 15 and 78 of the cumulative ^{39}Ar released, is 4.23 ± 0.03 Ga, and was probably reset by an impact event. With this interpretation, the fractional argon loss (F) from the low T phase is $\sim 90\%$, and that from the high T phase is $\sim 50\%$.

Overall, although the correction for recoiled ^{39}Ar may be somewhat subjective, it does provide a means by which to evaluate the quality of the age data. The considerable complexity of most of these spectra makes our interpretation of their Ar-Ar ages more uncertain than is the case for Ar-Ar analyses of many meteorites previously reported in the literature.

3.8. MIL99301 (LL6)

Interpretation of the Ar-Ar age spectrum for this meteorite is illustrative of the methodology we used in interpreting all of the age spectra. For this reason, and because we utilize the data for MIL99301 more extensively in a later discussion, we present a detailed interpretation of its Ar-Ar age spectrum here. Figure 1 is a plot of ^{39}Ar - ^{40}Ar age and K/Ca ratios vs. the cumulative fraction of ^{39}Ar released during stepwise temperature extractions of a whole-rock fragment of MIL99301. A substantial decrease in $^{36}\text{Ar}/^{38}\text{Ar}$ and $^{36}\text{Ar}/^{37}\text{Ar}$ ratios and ^{36}Ar concentrations (not shown) over the first several extractions indicates the release of adsorbed terrestrial Ar. We corrected for this atmospheric ^{40}Ar by using the $^{36}\text{Ar}/^{37}\text{Ar}$ ratio to apportion ^{36}Ar between air and cosmogenic fractions (Garrison et al., 2000). After such correction, a few low-temperature ages ($\leq 5\%$ ^{39}Ar release; Fig. 1) are still elevated, which we conclude is evidence of loss of some ^{39}Ar from grain surfaces during neutron irradiation. Between $\sim 5\%$ and 78% of the ^{39}Ar released, the K/Ca ratio is relatively constant and the age uniformly increases from 4.16 Ga to 4.26 Ga. This age increase is indicative of a small amount of diffusive loss of ^{40}Ar from feldspar grains. A very slight decrease in age for two extractions at $\sim 80\%$ ^{39}Ar released is probably due to release of ^{39}Ar that was recoil-implanted into grain surfaces of pyroxene during irradiation. Above 83% ^{39}Ar released, the Ar-Ar age rapidly increases to a pseudo-age plateau of ~ 4.52 Ga for four extractions releasing

11% of the total ^{39}Ar . Changes in the K/Ca ratio and the rate of release of ^{39}Ar with increasing extraction temperature indicate that those extractions above 83% ^{39}Ar release constitute a distinct K-bearing domain possessing different Ar diffusion properties. The entire Ar age spectrum does not resemble that expected for Ar loss from a single K-bearing phase.

We interpret this Ar-Ar age spectrum for MIL99301 as follows. The oldest age of ~ 4.52 Ga dates the time of postformational metamorphism of the parent body, which for type 6 chondrites occurred at temperatures of 820–930°C (Olsen and Bunch, 1984). The LL6 portion of the parent body in which MIL99301 resided then experienced significant heating in the thermal environment produced by an impact event between 4.20 and 4.26 Ga, where 4.20 Ga is the age shown by three extractions releasing 15–39% of the ^{39}Ar and 4.26 Ga is the age shown by two extractions releasing 67–78% of the ^{39}Ar (shown as shaded boxes in Fig. 1). The total summed age is 4.27 Ga. The exact time of this reheating event depends on whether the K-bearing phase releasing ~ 0 –83% of the ^{39}Ar was substantially or totally degassed by this heating event. By one interpretation, the event occurred at ~ 4.20 Ga, but incomplete degassing of this phase left some residual ^{40}Ar at intermediate extraction temperatures. Another interpretation is that the event occurred at ~ 4.26 Ga and Antarctic weathering decreased the age of lower temperature extractions. It is clear that this heating event only partially degassed Ar from the other K-bearing phase that degassed at higher temperatures between ~ 83 –100% ^{39}Ar released. A substantial impact on the LL parent body 4.23 ± 0.03 Ga is the only reasonable cause of a heating event so long after parent-body formation.

3.9. PCA91416 (LL6)

Redistribution of recoiled ^{39}Ar has altered the age spectrum of PCA91416 (Fig. 2a). The maximum age at intermediate temperatures, between 75% to 85% of the ^{39}Ar released, is ~ 4.22 Ga and probably represents degassing from interiors of feldspar grains relatively unaffected by ^{39}Ar recoil. This maximum age of 4.22 Ga is a lower limit to the early time of K-Ar closure and, assuming ^{40}Ar diffusion loss was minor, it may be a good measure of this time. This age is nearly identical to the total Ar-Ar age of 4.21 Ga summed across all extractions, and appears to indicate that no significant ^{39}Ar was lost from the sample during irradiation. The isochron gives a very large (4000) $^{40}\text{Ar}/^{36}\text{Ar}$ intercept. As we have eliminated air contamination, this can only be produced by excess ^{40}Ar at low-T, which greatly dominates over any ^{39}Ar recoil. Thus, we use the isochron slope and age to make the ^{39}Ar recoil correction, rather than the standard age spectrum method. Nevertheless, the corrected age spectrum (Fig. 2b) still shows relatively old ages for low-temperature extractions. In light of the considerable complexity in the interpretation of this age spectrum, we assume that Case 3 is correct, so that the peak age of 4.22 Ga is a lower limit, and consider that the total gas age of 4.21 Ga may not be valid (Table 2).

3.10. QUE97028 (LL5)

The age spectrum demonstrates obvious ^{39}Ar recoil effects (Fig. 2c). The total summed Ar-Ar age is 4.27 Ga. The inter-

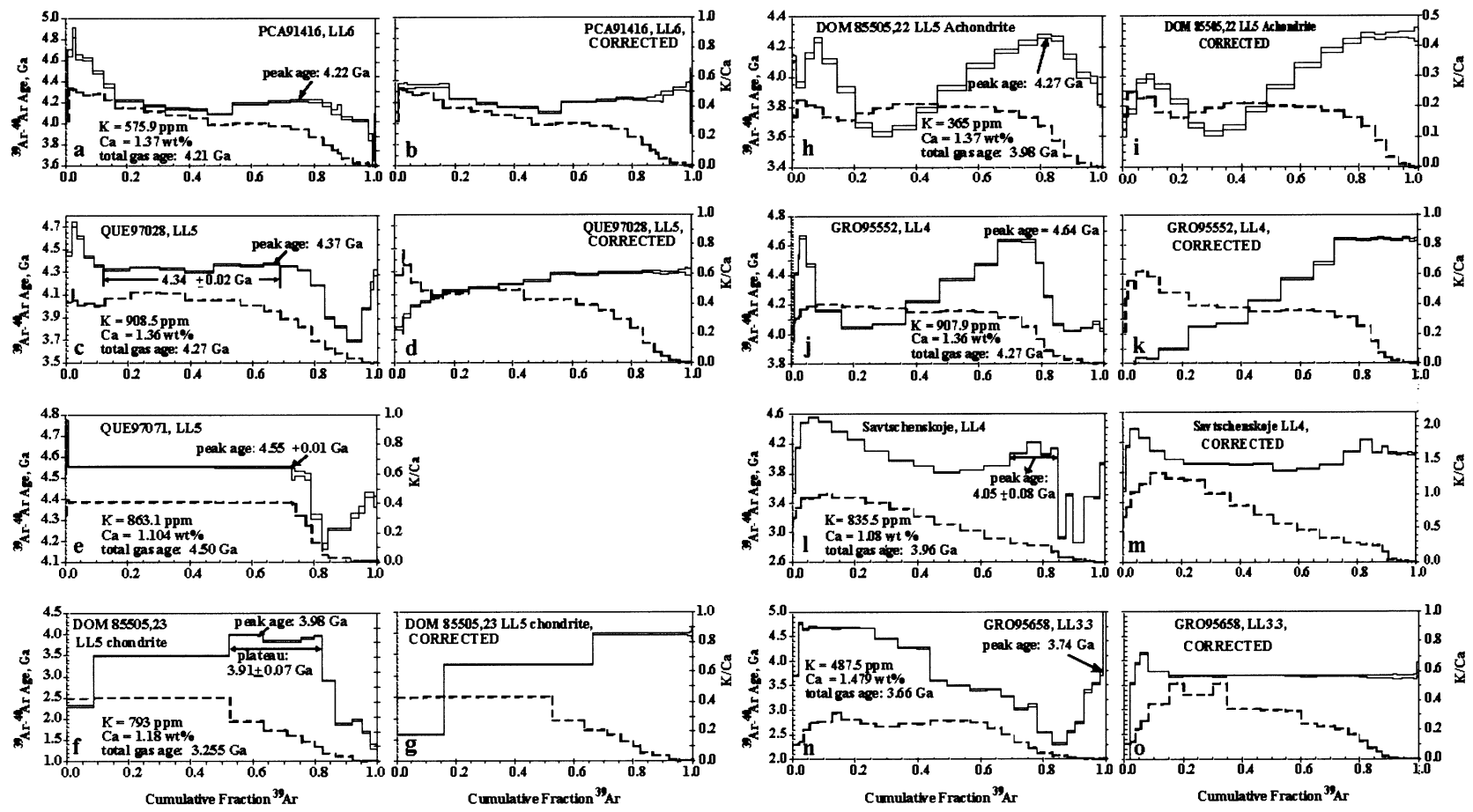


Fig. 2. (a-o) ^{39}Ar - ^{40}Ar age spectra for several LL-chondrites. Figures on the left for each meteorite are the measured ^{39}Ar - ^{40}Ar age spectra, showing age (rectangles, primary y-axis) and K/Ca ratio (dashed line, secondary y-axis) as a function of cumulative ^{39}Ar released. Figures on the right for each meteorite are corrected ^{39}Ar - ^{40}Ar age spectra, showing results of redistribution of recoiled ^{39}Ar from high T sites to low T sites. No corrected age spectrum is provided for QUE97071 (Fig. 2e) because this sample was accidentally overheated and $\sim 75\%$ of the ^{39}Ar was released in two extractions.

Table 2. ^{39}Ar - ^{40}Ar total gas and peak ages of the LL chondrites.

Sample	Description	Type	t_{tot} , Ga	t_{peak} , Ga	Case
MIL99301		LL6	≥ 4.27	4.52 ± 0.08 peak; 4.23 ± 0.03 average low T age; 4.26 ± 0.01 p-p	n.a.
PCA91416		LL6	disturbed	> 4.22	3
QUE97028		LL5	≥ 4.27	≥ 4.37 peak; 4.34 ± 0.02 p-p	2
QUE97071		LL5	≥ 4.50	≥ 4.55	n.d.
DOM85505,23	chondrite	LL5	≥ 3.26	≥ 3.98 peak $\geq 3.91 \pm 0.07$ p-p	2
DOM85505,22	igneous	LL5	disturbed	≥ 4.27	4
GRO95552		LL4	≥ 4.27	Disturbed	5
Savtschenskoje		LL4	≥ 3.96	≥ 4.23 peak; 4.05 ± 0.08 p-p	6
GRO95658		LL3.3	≥ 3.66	≥ 3.74	2

n.a.: not applicable; n.d.: not determined.

The term “pseudoplateau” abbreviated “p-p”, is used to describe two or more extractions from intermediate or high temperatures that have the same age within uncertainty of each other.

mediate portion of the age spectrum appears relatively undisturbed; 10 extractions releasing ~ 9 – 79% of the ^{39}Ar give a pseudoplateau age of 4.34 ± 0.02 Ga, and four extractions releasing ~ 47 – 74% of the ^{39}Ar give equal ages to each other within their respective uncertainties, with an average value of 4.36 ± 0.02 Ga. The peak age at high temperature (4.37 Ga) is greater than the total gas age, consistent with Case 2 described above. Unlike PCA91416, the isochron for QUE97028 has a significant negative intercept (-399), which strongly indicates effects of ^{39}Ar recoil, but not excess ^{40}Ar (Bogard and Garrison, 2003). Thus, for QUE97028 we used the standard age correction method described above. The corrected age spectrum provides no evidence for recoiled ^{39}Ar loss for this particular meteorite (Fig. 2d), and instead suggests diffusive loss of ^{40}Ar , consistent with the interpretations based on the uncorrected age spectrum and with the behavior described in Case 2 above. Thus, the total gas age of 4.27 Ga is likely to give a lower limit to the last time of major degassing; the pseudoplateau age of $\sim 4.34 \pm 0.02$ Ga likely represents the last time of significant Ar degassing for this meteorite (Table 2).

3.11. QUE97071 (LL5)

The third extraction of this chondrite was overheated accidentally and released 47% of the total ^{39}Ar (Fig. 2e). Nevertheless, we interpret the shape of this age spectrum (Fig. 2e) as likely having been affected throughout by ^{39}Ar recoil, and we adopt the total age to represent at least the minimum time of last Ar degassing, but possibly the actual degassing time. The total Ar-Ar age summed across all extractions is 4.5 Ga (Table 2). This age for QUE97071 is much older than those for QUE97028, and suggests that it experienced a different history from QUE97028, as well as from the other LL5 chondrites in this study, described below.

3.12. DOM85505,23 (LL5)

DOM85505,23 (LL5) is the chondritic host of an igneous melt fragment, DOM85505,22, described below (A. Reid; D. Mittlefehldt; T. McCoy, private communication). The age spectrum is highly disturbed, probably owing to a combination of diffusive loss of ^{40}Ar and recoil redistribution of ^{39}Ar (Fig. 2f). The total gas age is 3.26 Ga. Five extractions releasing ~ 52 –

82% of the ^{39}Ar define a pseudoplateau with an average age of 3.91 ± 0.07 Ga and a peak age of 3.98 Ga. This age is the minimum age for the last significant degassing of ^{40}Ar . The corrected age spectrum (Fig. 2g) uses the peak age of 3.98 Ga, and is consistent with Case 2, above. The total gas age thus provides a minimum estimate of the time of last major degassing (Table 2).

3.13. DOM85505,22 (LL5)

DOM85505,22 is an igneous-textured impact melt from host DOM85505,23. The ^{39}Ar - ^{40}Ar age spectrum indicates pervasive diffusive loss of ^{40}Ar and substantial redistribution of recoiled ^{39}Ar from the low- to the high-temperature extractions (Fig. 2h). The peak age of 4.27 Ga occurs at 80% of the ^{39}Ar release. The peak age is likely to be a minimum estimate of the true K-Ar age because of pervasive loss of ^{40}Ar , and is older than the peak age of its host (described above), as in the Peace River L6 chondrite where impact melt glass gave old ages due to retention of ^{40}Ar and loss of K during melting followed by rapid quenching (McConville et al., 1988). In contrast, the total Ar-Ar age of 3.98 Ga of this igneous sample is essentially identical to the peak age of its chondritic host. The corrected age spectrum (Fig. 2i) shows that even after redistribution of recoiled ^{39}Ar , the ages from low-temperature extractions are still relatively old. It appears that some recoiled ^{39}Ar that originated from these low-temperature extractions was lost from the sample, so that the total gas age may not provide a valid age (Case 4). Nevertheless, the peak age is probably a lower limit (Table 2).

3.14. GRO95552 (LL4)

The Ar-Ar age spectrum for this chondrite is very complex and indicates significant redistribution of recoiled ^{39}Ar . The age spectrum over ~ 10 – 70% ^{39}Ar release suggests some loss of ^{40}Ar by diffusion, but the anomalously old peak age of 4.64 Ga indicates loss of some recoiled ^{39}Ar from fine-grained K-bearing phases that degassed in the intermediate part of the age spectrum, as described in Case 5. Because the peak age is elevated, the corrected age spectrum (Fig. 2k) would overestimate the amount of recoiled ^{39}Ar . Nevertheless, because the corrected spectrum indicates that the ages are primarily af-

ected by diffusive loss of ^{40}Ar , the total summed Ar-Ar age of 4.27 Ga is probably a valid lower limit to the last time of major ^{40}Ar degassing (Table 2).

3.15. Savtschenskoje (LL4)

Savtschenskoje (LL4) also reveals an Ar-Ar age spectrum greatly influenced by ^{39}Ar recoil redistribution and likely ^{40}Ar diffusion loss. The peak age at high temperature (75% of the ^{39}Ar released) is equal to 4.23 Ga; the “plateau” age summed over 70% to 85% of the ^{39}Ar released is 4.05 ± 0.08 Ga, and the total gas age is 3.96 Ga (Fig. 2l). The corrected age spectrum (Fig. 2m) shows that the peak age is an average age from several extractions. We tentatively adopt the highest age of 4.23 Ga at $\sim 75\%$ release as the minimum time for the last major ^{40}Ar degassing. The corrected spectrum reveals relatively old ages from low-temperature extractions, indicating either that some ^{39}Ar was lost from the meteorite (Case 3) or some ^{39}Ar was implanted into low-K phases that degas at intermediate temperatures, thus lowering the peak age (Case 6). Savtschenskoje is most likely to exhibit the behavior described under Case 6, because first, unlike in Case 3, the pseudoplateau age of 4.05 ± 0.08 Ga exceeds the total gas age of 3.96 Ga. Second, as in Case 6, the K/Ca ratio decreases in a stepwise fashion from low- to high-temperature extractions, suggesting that a mixture of feldspar and pyroxene degasses over a large range of temperatures. Thus, the total gas age of 3.96 Ga and peak age of 4.05 Ga are likely to be lower limits (Table 2).

3.16. GRO95658 (LL3.3)

The age spectrum shown in Figure 2n has been corrected for terrestrial ^{40}Ar . The corrected data over $\sim 2\text{--}26\%$ of the ^{39}Ar release define an elevated pseudoplateau age of ~ 4.60 Ga and suggest that low-temperature loss of ^{40}Ar probably was not extensive. This elevated age, compared with the much younger ages at higher extraction temperatures, indicates recoil loss of ^{39}Ar from grain surfaces. Similarly, the deep minimum in the age spectrum over $\sim 78\text{--}93\%$ of the ^{39}Ar release, at a point in the release where the K/Ca ratio decreases substantially, is consistent with gain of recoiled ^{39}Ar in pyroxene grain surfaces. Because redistribution of recoiled ^{39}Ar is so extensive in this meteorite, it is very difficult to derive an Ar degassing age. The corrected age spectrum (Fig. 2o) shows a relatively flat profile, with a few low-temperature extractions having relatively old ages, suggesting very minor ^{39}Ar recoil loss. Thus, the age spectrum is most consistent with behavior described in Case 2, plus very minor recoil ^{39}Ar loss. Because of some evidence for diffusive ^{40}Ar loss, the peak age of 3.74 Ga is probably a minimum age. In conjunction with the very minor amount of ^{39}Ar loss, this observation suggests that the total gas age of 3.66 Ga is a minimum estimate of the time the meteorite cooled (Table 2).

In summary, the maximum age at high temperatures, defined as the peak age (t_{peak} in Table 2), is greater than or equal to the total gas age (t_{tot}) for all samples because t_{tot} includes the low-temperature release steps that are typically affected by diffusive loss of ^{40}Ar during cooling of the meteorite. Because the age spectra of GRO95552 is highly disturbed by ^{39}Ar recoil loss, t_{peak} does not provide a good age estimate, and conse-

quently only t_{tot} is reported in Table 2. The age spectra of PCA91416 and DOM85505,22 reveal possible recoiled ^{39}Ar loss, so only the peak age is reported in Table 2. Finally, the age spectra of QUE97208, DOM85505,23, Savtschenskoje, and MIL99301 show smaller recoil effects, and although the peak age may have been lowered by diffusive loss of ^{40}Ar , it is unlikely to have been elevated by recoiled ^{39}Ar . Thus, both t_{peak} and t_{tot} are reported for these meteorites in Table 2, and these ages should be considered minimum estimates.

4. DISCUSSION

The observation that almost all of these LL-chondrites, comprising various metamorphic grades, show significant ^{39}Ar recoil effects, indicates that much of the K is located in very fine-grained, possibly interstitial phases. In this regard, these LL-chondrites show similar ^{39}Ar recoil effects to published Ar-Ar analyses for L3 and L4 chondrites (Stephan and Jessberger, 1988; Kaneoka, 1981), H3 chondrites (Sainte Rose) (Stephan and Jessberger, 1992), and some LL4 and LL5 chondrites (Bernatowicz et al., 1988). The large amount of ^{39}Ar recoil redistribution makes it difficult to model the last times of significant K-Ar chronometer resetting of LL-chondrites. To the extent that recoiled ^{39}Ar was retained in these samples, the total age summed across all extractions may date this last Ar degassing event. In those cases where later diffusive loss of ^{40}Ar is indicated, the total Ar age appears to be a lower limit to the last time of major degassing. For some meteorites, suggestions of an age plateau at intermediate extraction temperatures, at a point in the age spectrum where ^{39}Ar recoil effects are expected to be minimal, may date an Ar degassing event.

Despite the complexity in the age spectra of most of the meteorites in this study, some interesting inferences about the LL chondrite parent body history may be drawn from their petrographic types, shock stages, and ages. One important observation is that, as shown in Table 2, there is no systematic correlation between the peak or total gas age and the metamorphic type. Thus, these data do not shed light on the question of whether the LL-chondrite parent body had an onion-shell type structure. Nevertheless, if the LL parent body does indeed have an onion-shell structure (Pellas et al., 1990), our results from MIL99301, and previous results from Olivenza (Turner and Cadogan, 1973; Turner et al., 1978) may not support previous interpretations for very slow cooling of the LL5-LL6 regions of the parent body over 200–230 Ma (Pellas et al., 1990). Even considering the possibility that the oldest LL6 age of 4.52 ± 0.08 Ga (MIL99301, high-temperature extractions) and LL5 age of 4.53 ± 0.16 Ga (Olivenza) (Turner and Cadogan, 1973; Turner et al., 1978) are partly reset by early impacts, the ages are consistent (within rather large uncertainties) with cooling of the LL5-LL6 regions of the parent body in as little as 20 to 30 Ma. Less metamorphosed (LL3) regions of the LL parent body were interpreted to have cooled more rapidly over only ~ 50 Ma (i.e., 4.55 Ga to 4.50 ± 0.05 Ga, ALHA77304) (Kaneoka, 1980). These estimates suggest that cooling occurred more rapidly than the 200–230 Ma duration suggested by previous studies, and would imply the LL body was smaller than previously thought.

The second important observation is that three out of eight meteorites (not including the igneous melt inclusion,

DOM85505,22) have total gas ages close to 4.27 Ga (GRO95552, QUE97028, MIL99301) (Table 2). These three meteorites have a range of petrographic types including 4, 5, and 6. In addition to MIL99301 having a total gas age of 4.27 Ga, a pseudo-plateau in MIL99301 also records the timing of an impact event at $\sim 4.26 \pm 0.01$ Ga. The similarity in the total gas ages of these three meteorites suggests that either the ages were reset at this time by heating produced by a rather large impact event that affected most of the parent body, or that there were a number of smaller impacts at about this time. The suggestion from the present study of significant impact(s) at around 4.27 Ga is consistent with results from previous studies on three LL chondrites (Uden, Trebbin, and Bhola) that have ages near 4.2 Ga (Trieloff et al., 1989; Trieloff et al., 1994). (Note that these ages for Uden, Trebbin, and Bhola are conventional plateau ages, but like the results from this study, their spectra are characterized by ^{39}Ar recoil-induced disturbances in the high-temperature extractions. M. Trieloff, private communication).

Based on these observations, a number of scenarios can be envisioned to produce the range of ^{39}Ar - ^{40}Ar ages observed in these LL-chondrites. First, it seems reasonable to propose that the age spectra of some meteorites, such as MIL99301, have been completely or partly reset to the time of impact at around 4.27 Ga owing to relatively rapid initial cooling within a regolith layer. Second, comparing the ages of the LL5 chondrites (Table 2) shows that their maximum ages from high-temperature extractions differ (≥ 4.37 , ≥ 4.55 , ≥ 4.27 , ≥ 3.98 Ga), as do their total gas ages (≥ 4.27 Ga, ≥ 4.50 Ga [disturbed], and ≥ 3.26 , respectively). In light of other evidence for an impact at ~ 4.27 Ga, it seems unlikely that QUE97028 lost some ^{40}Ar by later diffusion to produce a K-Ar age of 4.27 Ga only by coincidence. Thus, meteorites with K-Ar ages of 4.27 Ga may have been excavated and then cooled rapidly at this time. Third, other meteorites, that have older ages > 4.27 Ga, may have been unaffected or only partly reset by impacts at this time. Finally, some meteorites (e.g., GRO95658) may have been more deeply buried within regolith blankets following the ~ 4.27 Ga impacts, and experienced relatively slow cooling to produce ages younger than ~ 4.27 Ga. Alternatively, they may have been reset by substantially later impact events (Nakamura and Okano, 1985). The total gas age of 3.66 Ga for the LL3.3 meteorite (GRO95658) is much younger than the total gas ages of the LL4 meteorites, Savtschenskoje, 3.96 Ga and GRO95552, 4.27 Ga. Yet, by definition, the LL3 chondrite is essentially unmetamorphosed, so would be expected to have an older total gas age than the LL4 chondrites. The lower shock stage (S2) of the LL3 chondrite may also suggest it should have experienced less shock-induced heating and ^{39}Ar - ^{40}Ar age resetting than the LL4 chondrite (S3), although there is not always a direct correlation between the shock stage and the extent of resetting of the Ar-Ar age (Jessberger and Ostertag, 1982). These factors, as well as the 610 Ma difference in total gas ages between the LL3.3 GRO95658 and the LL4 GRO95552 suggest that the LL3.3 GRO95658 experienced a much later impact event at < 4.0 Ga.

4.1. Implications of Annealing

Although the highest temperature Ar-Ar ages from MIL99301 were not completely reset, the shock features in feldspar were completely annealed to a low shock stage of S1 (Rubin, 2002). We conclude that feldspar annealing (following some earlier impact event) did not occur before the major impact event, because if MIL99301 had been substantially reshocked *after* it was annealed, the shock stage would be greater than S1. The relative temperature and time required to anneal the feldspar, compared with those needed to reset the ^{39}Ar - ^{40}Ar ages, can thus be inferred from the age spectrum of MIL99301. Apparently, the temperature and/or time required to anneal feldspar are less than those required for complete resetting of the entire ^{39}Ar - ^{40}Ar age spectrum. One possibility is that the meteorite experienced a peak temperature that was insufficient to reset the Ar-Ar ages of the feldspar phases that degas at the highest temperatures, but that was nevertheless high enough to permit annealing of all the feldspar grains. A second is that, for a given temperature initially above the blocking temperature of Ar in feldspar, the time required to heal crystallographic defects in feldspar is shorter than the time required for complete argon loss from feldspar by diffusion. A third is that the temperature was initially above the blocking temperature of argon in feldspar, but subsequently decreased to where annealing occurred but Ar diffusion did not. In the next section, we will model the thermal conditions produced in the vicinity of the impact on MIL99301 that apparently caused annealing but that were insufficient to completely reset the ^{39}Ar - ^{40}Ar ages.

Further insights into the conditions required for resetting of the Ar-Ar age compared with that for annealing may be obtained by comparison of MIL99301 and PCA91416 (LL6), that have very different apparent shock stages. In contrast to MIL99301, PCA91416 is not annealed, has a much higher apparent shock stage (S4), implying higher temperatures, and yet has a somewhat younger peak age (4.22 Ga). However, the general similarity between the peak age of PCA91416 and the secondary pseudoplateau age of MIL99301 (4.22 and 4.26 ± 0.01 Ga, respectively) is consistent with resetting by impact events that occurred at about the same time. The results from PCA91416 suggest that although the energy of impact was quite high (S4), the postimpact conditions were not conducive to annealing, possibly owing to relatively rapid cooling. Thus, in the case of MIL99301, even if the initial temperature was relatively high and the initial cooling rate was rapid as suggested by our model below, a period of burial to permit annealing seems to be required. In summary, these observations appear to favor prolonged burial following impact, over relatively hot impact-induced heating alone, as conditions required to permit annealing, although further evidence is needed.

4.2. Thermal Model for MIL99301

The results from MIL99301 can be used to construct a model of its thermal history. We used the ^{39}Ar abundances as a function of stepwise temperature release to calculate diffusion parameters D/a^2 for our sample of MIL99301 (Fechtig and Kalbitzer, 1966). By making certain simplifying assumptions, we can utilize the Ar diffusion data for MIL99301 to construct

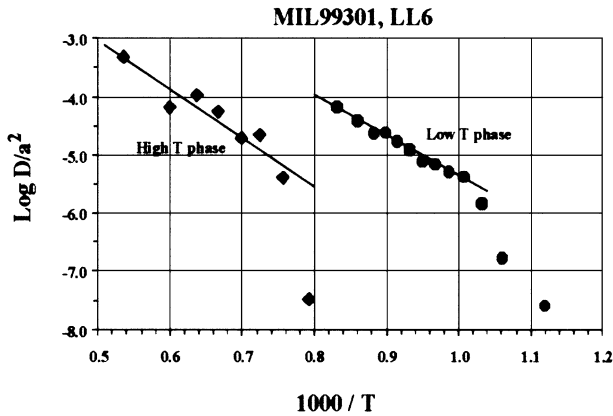


Fig. 3. Arrhenius plot of diffusion parameter D/a^2 vs. reciprocal temperature (in Kelvin). The ^{39}Ar that degasses from two distinct Ar diffusion domains is plotted separately: (1) a low-temperature phase, from 0 to 83% ^{39}Ar , with an activation energy of 34 kcal/mol, and (2) a high-temperature phase, from 83–100% ^{39}Ar , with an activation energy of 38 kcal/mol.

a thermal model that constrains the postshock thermal environment of MIL99301 on the parent asteroid. This model combines the thermal cooling times of slabs of varying thicknesses with the times required to lose some fraction of the total Ar from a sample as a function of Ar diffusivity, D/a^2 . We assume that the impact event which produced the shock features in MIL99301 uniformly heated a zone beneath the crater to an initial temperature of $\sim 600^\circ\text{C}$. This temperature derives from petrographic observations (Rubin, 2002) that the postshock metamorphism experienced by MIL99301 did not exceed conditions experienced by type-4 chondrites (Dodd, 1969; Dodd, 1981; Dodd and Jarosewich, 1979), although the degree of metamorphism may have been lower (Rubin, 2002). From extrapolations of the linear trends defined by the Arrhenius data for ^{39}Ar to a temperature of 600°C , we obtain values for D/a^2 of $\sim 3 \times 10^{-7}$ for the low-temperature, K-bearing phase and $\sim 3 \times 10^{-9}$ for the high-temperature phase (Fig. 3). We note from the Ar age spectrum (Fig. 1) that the low-T phase apparently lost $>90\%$ of its radiogenic ^{40}Ar at 4.20–4.26 Ga, and that the high-T phase apparently lost $\leq 50\%$ of its radiogenic ^{40}Ar at this time.

Collectively the Ar isotopic data from MIL99301 indicate that the first several extractions (0–5% of the ^{39}Ar) contain terrestrial Ar and were released from a weathering phase. The calculated activation energy for these data is quite low, ~ 14 kcal/mol, and they are omitted from further consideration. The remaining Ar data indicate that ^{39}Ar release occurred from two distinct diffusion domains. Separate D/a^2 calculations were made for the phase releasing 5–83% of the total ^{39}Ar and the phase releasing 83–100% of the ^{39}Ar . An Arrhenius plot of D/a^2 vs. reciprocal temperature for the lower temperature phase is linear for 10 extractions releasing ~ 20 –83% of the total ^{39}Ar , and yields an Ar activation energy of ~ 34 kcal/mol (Fig. 3). The higher T phase gives a roughly linear, but less well-defined Arrhenius plot that is offset toward lower D/a^2 values compared with the low-T phase (Fig. 3). The Ar activation energy for the high-T phase, ~ 38 kcal/mol, is only slightly higher than that for the low-T phase. This suggests that the different Ar diffusion characteristics of the two K-bearing

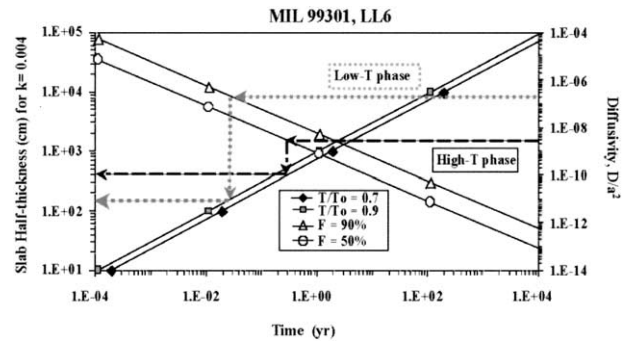


Fig. 4. A model for the postimpact thermal environment of MIL99301, which relates the cooling times of the center of linear impact deposits of varying thicknesses (left scale) with the times required to produce specified amounts of fractional Ar loss as a function of Ar diffusivity, D/a^2 (right scale). The two curves shown for thermal cooling assume T/T_0 values of 0.9 and 0.7, where T is temperature. The two curves shown for Ar diffusion define Ar losses of 90% and 50%. We assume a reheating temperature for MIL99301 of 600°C , for which the values of D/a^2 for the low-T phase (50% ^{40}Ar loss) and the high-T phases (90% loss) are $\sim 3 \times 10^{-7}$ and $\sim 3 \times 10^{-9}$, respectively, and are shown by the dashed lines intersecting the D/a^2 scale. Because the Ar diffusion and thermal cooling curves must define a common time, these two values of D/a^2 define half-thicknesses for the impact deposits of ~ 1.5 m and ~ 4 m for the low-T and high-T phases, respectively. Thus, Ar data for MIL99301 are consistent with its residence in a relatively hot deposit several meters in thickness, produced by an impact of moderate size, that cooled at a relatively rapid rate of $\sim 10^{-3}^\circ\text{C/s}$.

phases are produced by different mean grain sizes or crystal structures, possibly the result of the second annealing phase, rather than significantly different mineralogy. This interpretation is consistent with petrographic observations described above, and with experimental work (Keck et al., 1986) that showed annealing can cause low-temperature feldspar to be converted into higher temperature (disordered) feldspar.

Figure 4 shows the model relationship for the time required to lose 90% and 50% of an initial concentration of Ar as a function of Ar diffusivity, D/a^2 . Figure 4 also shows the time required for a slab with a thermal diffusivity of $0.004\text{ cm}^2/\text{s}$ to cool to 90% and 70% of its initial temperature ($T/T_0 = 0.9$ and 0.7). These relationships are based on similar models presented by Bogard et al. (1976) and Nyquist et al. (1979). The horizontal dashed lines in Figure 4 represent the D/a^2 values at 600°C for the two K-bearing phases in MIL99301. The times required to produce the fractional Ar losses observed in the low-T and high-T phases are given by the intersection of these dashed lines with the model lines representing 90% and 50% Ar diffusion loss. These times are ~ 0.02 yr and ~ 0.2 yr for the low- and high-temperature phases, respectively. If we then extend the dashed lines downward to intersect the model curves for cooling of a slab, we can read on the left y-axis the required half-thickness of slabs that cool during these time periods to 90% and 70% of their initial temperature. Because cooling of a system occurs more rapidly in its initial phase and because the K-Ar chronometer is expected to close at a relatively high temperature in systems cooling as rapidly as MIL99301, we adopt the model curve for $T/T_0 = 0.9$. These slab half-thicknesses are ~ 1.5 m and ~ 4 m. Note that if we had adopted $T/T_0 = 0.7$, the slab thicknesses would be only slightly less.

From the model considerations described above, the thickness of the hot ejecta layer that contained MIL99301 immediately after the parent body impact at 4.26 ± 0.01 Ga was ~ 3 m from the low-T data and ~ 8 m from the less precise high-T data. We prefer the value of ~ 3 m, and differences between these numbers possibly reflect uncertainties in the Ar diffusion data used and in the estimated fractional degassing of ^{40}Ar . Although this calculation makes the simplifying assumptions that first, the heated impact material can be treated as a hot layer bordered by cold host material, and second, that it resided in a uniformly heated unit beneath the crater (whereas in reality impact heating of crater deposits was probably heterogeneous), the model does support the scenario that after impact, MIL99301 was heated to $\sim 600^\circ\text{C}$ and resided a few meters beneath the crater floor. The initial cooling rate after impact would have been relatively fast, so that the K-Ar chronometer would have become closed to diffusive Ar loss relatively early in the cooling process. These characteristics seem completely consistent with ejecta from an impact of moderate size on the LL asteroid parent body.

4.3. Observed vs. Experimental Annealing Conditions and Possible Implications for Parent Body History

Observations from several annealed meteorites appear to suggest that heating to type 4–6 conditions is required (Rubin, 2002). Annealing of olivine and feldspar in MIL99301 apparently occurred at temperatures less than or equal to petrographic type-4 conditions (600°C) (Rubin, 2002). Some previous experimental work designed to clarify the annealing process in meteorites showed that shock-induced olivine microfractures could be annealed in 20 min at $700\text{--}900^\circ\text{C}$ (Bauer, 1979), or 90 h at 900°C (Ashworth and Mallinson, 1985). However, because these experiments were performed at relatively high temperatures and over short time periods that may not be representative of the range of possible conditions on ordinary chondrite parent bodies, they therefore do not preclude that damaged olivine and feldspar crystal lattices were healed at lower temperatures over relatively long time periods, as is suggested by other annealing studies performed at 400°C over 10 h (Guimon et al., 1985).

Although some of the meteorites in the present study were clearly influenced by relatively late impacts, our observations raise the question as to whether we can distinguish between the following two general situations: (1) very early impact events (close to 4.5 Ga) produced relatively high shock stages and reset $^{39}\text{Ar}\text{--}^{40}\text{Ar}$ ages of some meteorites, but subsequent burial within regolith layers caused olivine and feldspar to be annealed to shock stage S1; (2) as described in (1), but evidence for shock was instead annealed by heat produced from decay of extinct radionuclides. It appears these possibilities may not be distinguished unless there is independent evidence for the cooling rate (e.g., Trierloff et al., 2003). In theory, meteorites having low shock stages of S1 and reset $^{39}\text{Ar}\text{--}^{40}\text{Ar}$ ages may be associated with Pb-Pb ages that have not been reset. This is largely because for a given cooling rate, the Pb-Pb chronometer has a higher closure temperature in phosphates ($\sim 550^\circ\text{C}$ to 900°C , depending on cooling rate, e.g., Renne, 2000; Sano et al., 2000) than does the $^{39}\text{Ar}\text{--}^{40}\text{Ar}$ system in feldspar (Renne, 2000).

5. CONCLUSIONS

It is often assumed that those Ar-Ar ages of chondrites that are $\sim 0.1\text{--}0.3$ Ga younger than the accepted time of parent body formation at ~ 4.56 Ga were produced by slow cooling deep within the parent body. Our studies on LL-chondrites suggest that heating by early impacts may also have played an important role in resetting the Ar-Ar ages of chondrites. Our $^{39}\text{Ar}\text{--}^{40}\text{Ar}$ age dating of some LL chondrites supports an impact event at around 4.27 Ga on the LL parent asteroid that reset the age of some meteorites and produced local impact melts, and may have also exhumed (or buried) others to produce a range of cooling ages. This process has been modeled for MIL99301, and suggests that, following an impact at $\sim 4.23 \pm 0.03$ Ga that produced the secondary metamorphism, MIL99301 resided several meters beneath the floor of a medium-sized crater on the LL parent body. The $^{39}\text{Ar}\text{--}^{40}\text{Ar}$ ages are therefore consistent with a previous study that suggested postshock annealing of K-bearing feldspar to a shock grade of S1 in MIL99301. The LL4, 5 chondrites GRO95552 and QUE97028 have similar K-Ar ages of ~ 4.27 Ga, and may have been exhumed by impact events at around this time. The impact melt DOM85505,22 has a peak age of ≥ 4.27 Ga, and therefore formed no later than the time of the impact event that partly reset MIL99301. In contrast, the comparatively young peak age of 3.74 Ga from GRO95658 (LL3.3) suggests an additional impact event at < 4.0 Ga, possibly close to the time of impact reset ages of a few other ordinary chondrites between 3.6–3.8 Ga (Bogard, 1995). Despite the apparently extensive early impact-resetting of some of the LL chondrites in this study, some highly metamorphosed regions of the parent body preserve relatively old ages, such as QUE97071 (LL5), with a total age of ≥ 4.50 Ga, and Olivenza, with a plateau age of 4.53 ± 0.16 Ga (Turner and Cadogan, 1973; Turner et al., 1978). These equilibrated meteorites with old ages may have implications for the early cooling history of the LL chondrite parent body if it had an onion-shell type structure (Pellas et al., 1990), because they suggest the LL-parent body was smaller than previously suggested.

We do not observe a strong correlation between the petrographic type and the age of these LL chondrites that would be predicted by the onion-shell model. Instead, our results suggest that in many cases, the original relationships between the age and the degree of metamorphism have been obscured by impact-induced resetting at ~ 4.27 Ga. Some meteorites appear to have been cooled rapidly after impacts, whereas others may have been buried and cooled more slowly to produce somewhat younger K-Ar ages. The results from MIL99301 suggest an Ar closure temperature of $\sim 600^\circ\text{C}$, implying that annealing of feldspar and olivine can occur at relatively low temperatures corresponding to type-4 metamorphic conditions, or possibly still lower temperatures ($\leq 400^\circ\text{C}$) as shown by previous experimental studies. This suggests that apparently unshocked meteorites may have reset $^{39}\text{Ar}\text{--}^{40}\text{Ar}$ ages. These findings may have implications for other studies that utilize apparently unshocked ordinary chondrites to model the thermal history of asteroidal parent bodies. Careful petrographic analysis may be needed to evaluate the possible extent of postshock annealing.

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REFERENCES

- Anders E. (1978) Most stony meteorites come from the asteroid belt. In *Asteroids: An Exploration Assessment* (eds. D. Morrison and W. C. Wells), pp. 57–75. NASA.
- Ashworth J. R. and Mallinson L. G. (1985) Transmission electron microscopy of L-group chondrites, 2: Experimentally annealed Kyushu. *Earth Planet. Sci. Lett.* **73**, 33–40.
- Bauer J. F. (1979) Experimental shock metamorphism of mono- and polycrystalline olivine: A comparative study. *Proc. Lunar Planet. Sci. Conf.*, 2573–2596.
- Bernatowicz T. J., Podosek F. A., Swindle T. D., and Honda M. (1988) I-Xe systematics in LL chondrites. *Geochim. Cosmochim. Acta* **52**, 1113–1121.
- Bogard D. D. (1995) Impact ages of meteorites: A synthesis. *Meteoritics* **30**, 244–268.
- Bogard D. D. and Garrison D. H. (2003) ^{39}Ar - ^{40}Ar ages of eucrites and thermal history of asteroid 4 Vesta. *Met. Planet. Sci.* **38**, 669–710.
- Bogard D. D., Garrison D. H., and McCoy T. J. (2000) Chronology and petrology of silicates from IIE iron meteorites: Evidence of a complex parent body evolution. *Geochim. Cosmochim. Acta* **64**, 2133–2154.
- Bogard D. D. and Hirsch W. C. (1980) ^{40}Ar / ^{39}Ar dating, Ar diffusion properties, and cooling rate determinations of severely shocked chondrites. *Geochim. Cosmochim. Acta* **44**, 1667–1682.
- Bogard D. D., Husain L., and Nyquist L. E. (1979) ^{40}Ar - ^{39}Ar age of the Shergotty achondrite and implications for its post-shock thermal history. *Geochim. Cosmochim. Acta* **43**, 1047–1055.
- Bogard D. D., Husain L., and Wright R. J. (1976) ^{40}Ar - ^{39}Ar dating of collisional events in chondrite parent bodies. *J. Geophys. Res.* **81**, 5664–5678.
- Dixon E. T., Bogard D. D., and Garrison D. H. (2003) ^{39}Ar - ^{40}Ar chronology of R-chondrites. *Met. Planet. Sci.* **38**, 341–356.
- Dodd R. T. (1969) Metamorphism of the ordinary chondrites: A review. *Geochim. Cosmochim. Acta* **33**, 161–203.
- Dodd R. T. (1981) *Meteorites: A Petrologic-Chemical Synthesis*. Cambridge University Press, Cambridge.
- Dodd R. T. and Jarosewich E. (1979) Incipient melting in and shock classification of L-group chondrites. *Earth Planet. Sci. Lett.* **44**, 335–340.
- Fechtig H. and Kalbitzer S. (1966) The diffusion of argon in potassium-bearing solids. In *Potassium-Argon Dating*, pp. 68–107. Springer-Verlag.
- Garrison D., Hamlin S., and Bogard D. (2000) Chlorine abundances in meteorites. *Met. Planet. Sci.* **35**, 419–429.
- Grimm R. E. (1985) Penecontemporaneous metamorphism, fragmentation, and reassembly of ordinary chondrite parent bodies. *J. Geophys. Res.* **90**, 2022–2028.
- Guimon R. K., Keck B. D., Weeks K. S., Dehart J., and Sears D. W. G. (1985) Chemical and physical studies of type 3 chondrites—IV: Annealing studies of a type 3.4 ordinary chondrite and the metamorphic history of meteorites. *Geochim. Cosmochim. Acta* **49**, 1515–1524.
- Hohenberg C. M., Hudson B., Kennedy B. M., and Podosek F. A. (1981) Noble gas retention chronologies for the St. Severin meteorite. *Geochim. Cosmochim. Acta* **45**, 535–546.
- Huenke J. C. and Smith S. P. (1976) ^{39}Ar recoil out of small grains and implications for ^{40}Ar - ^{39}Ar dating. *Lunar Planet. Sci. Conf.*, 7th, 1987–2008.
- Jessberger E. K. and Ostertag R. (1982) Shock-effects on the K-Ar system of plagioclase feldspar and the age of anorthosite inclusions from North-Eastern Minnesota. *Geochim. Cosmochim. Acta* **46**, 1465–1471.
- Kaneoka I. (1980) ^{40}Ar - ^{39}Ar ages of L and LL chondrites from Allan Hills, Antarctica: ALHA77015, 77214 and 77304. *Symp. Antarctic Meteorites*, 5th, No. 17, 177–188.
- Kaneoka I. (1981) ^{40}Ar - ^{39}Ar ages of Antarctic meteorites: Y-74191, Y-75258, Y-7308, Y-74450 and ALH-765. *Symp. Antarctic Meteorites*, 6th, No. 20, 250–263.
- Keck B. D., Guimon R. K., and Sears D. W. G. (1986) Chemical and physical studies of type 3 chondrites. VII -Annealing studies of the Dhajala H3.8 chondrite and the thermal history of chondrules and chondrites. *Earth Planet. Sci. Lett.* **77**, 418–427.
- Keil K., Haack H., and Scott E. R. D. (1994) Catastrophic fragmentation of asteroids: Evidence from meteorites. *Planet. Space Sci.* **42**, 1109–1122.
- Lipschutz M. E., Gaffey M. J., and Pellas P. (1989) Meteoritic parent bodies: Nature, number, size and relation to present-day asteroids. In *Asteroids II* (eds. R. P. Binzel, T. Gehrels, and M. S. Matthews), pp. 740–777. University of Arizona Press.
- McConville P., Kelley S., and Turner G. (1988) Laser probe ^{40}Ar - ^{39}Ar studies of the Peace River shocked L6 chondrite. *Geochim. Cosmochim. Acta* **52**, 2487–2499.
- McDougall I. and Harrison T. M. (1999) *Geochronology and Thermochronology by the ^{40}Ar / ^{39}Ar Method*. Oxford University Press, 269 pp.
- Minster J.-F. and Allegre C. J. (1979) ^{87}Rb - ^{86}Sr chronology of H chondrites: Constraints and speculations on the early evolution of their parent body. *Earth Planet. Sci. Lett.* **42**, 333–347.
- Nakamura N. and Okano O. (1985) 1,200-Myr impact-melting age and trace-element chemical features of the Yamato-790964 chondrite. *Nature* **315**, 563–566.
- Nyquist L., Wooden J., Bansal B., Wiesmann H., McKay G., and Bogard D. (1979) Rb-Sr ages of the Shergotty achondrite and implications for the metamorphic resetting of isochron ages. *Geochim. Cosmochim. Acta* **43**, 1057–1074.
- Olsen E. J. and Bunch T. E. (1984) Equilibration temperatures of the ordinary chondrites: A new evaluation. *Geochim. Cosmochim. Acta* **48**, 1363–1365.
- Pellas P. (1982) Early thermal histories of L chondrites. *Lunar Planet. Sci. Conf.*, 825–827.
- Pellas P. and Fieni C. (1988) Thermal histories of ordinary chondrite parent asteroids. *Lunar Planet. Sci. XIX* **19**, 915–916.
- Pellas P., Fieni C., Trieloff M., and Jessberger E. K. (1990) Metamorphism intervals of equilibrated H and LL chondrites as defined by ^{244}Pu chronometry and ^{40}Ar - ^{39}Ar ages. *Meteoritics* **25**, 397.
- Pellas P. and Storzer D. (1981) ^{244}Pu fission track thermometry and its application to stony meteorites. *Proc. Royal Soc. London* **374**, 253–270.
- Renne P. R. (2000) ^{40}Ar - ^{39}Ar age of plagioclase from Acapulco meteorite and the problem of systematic errors in cosmochronology. *Earth Planet. Sci. Lett.* **175**, 13–26.
- Rubin A. E. (2002) Post-shock annealing of Miller Range 99301 (LL6): Implications for impact heating of ordinary chondrites. *Geochim. Cosmochim. Acta* **66**, 3327–3337.
- Sano Y., Terada K., Takeno S., Taylor L. A., and McSween H. Y. (2000) Ion microprobe uranium-thorium-lead dating of Shergotty phosphates. *Met. Planet. Sci.* **35**, 341–346.
- Scott E. R. D. (2003) Metallographic cooling rates of H chondrites and the structure of their parent body. *Met. Planet. Sci.* **38**, A151.
- Scott E. R. D. and Rajan R. S. (1979) Thermal history of the Shaw chondrite. *Proc. Lunar Planet. Sci. Conf.* **10th**, 1031–1043.
- Scott E. R. D. and Rajan R. S. (1981) Metallic minerals, thermal histories, and parent bodies of some xenolithic, ordinary chondrites. *Geochim. Cosmochim. Acta* **45**, 53–67.
- Stephan T. and Jessberger E. K. (1988) ^{40}Ar - ^{39}Ar ages of types 3 and 4, L and H chondrites from Antarctica. *Meteoritics* **23**, 373.
- Stephan T. and Jessberger E. K. (1992) ^{40}Ar - ^{39}Ar dating of the H3 chondrite Sainte Rose. *Meteoritics* **27**, 580–584.
- Stoffer D., Keil K., and Scott E. R. D. (1991) Shock metamorphism of ordinary chondrites. *Geochim. Cosmochim. Acta* **55**, 3845–3867.

- Taylor G. J., Maggiore P., Scott E. R. D., Rubin A. E., and Keil K. (1987) Original structures, and fragmentation and reassembly histories of asteroids: Evidence from meteorites. *Icarus* **69**, 1–13.
- Trieloff M., Jessberger E. K., Herrwerth I., Hopp J., Fieni C., Ghelis M., Bourot-Denise M., and Pellas P. (2003) Structure and thermal history of the H-chondrite parent asteroid revealed by thermochronometry. *Nature* **422**, 502–506.
- Trieloff M., Jessberger E. K., and Oehm J. (1989) Ar-Ar ages of LL chondrites. *Meteoritics* **24**, 332.
- Trieloff M., Kunz J., and Jessberger E. K. (1994) High-resolution ^{40}Ar - ^{39}Ar dating of K-rich chondritic inclusions. *57th Annu. Mtg. Met. Soc.*, 541.
- Turner G. and Cadogan P. H. (1973) ^{40}Ar - ^{39}Ar chronology of chondrites. *Met. Soc.*, *35th*, 447–448.
- Turner G. and Cadogan P. H. (1974) Possible effects of ^{39}Ar recoil in ^{40}Ar - ^{39}Ar dating. *Proc. Lunar Sci. Conf. 5th*, 1601–1615.
- Turner G., Enright M. C., and Cadogan P. H. (1978) The early history of chondrite parent bodies inferred from ^{40}Ar - ^{39}Ar ages. *Proc. Lunar Planet. Sci. Conf. 9th*, 989–1025.