T-2414

THE U-Pb AGE OF L CHONDRITES DETERMINED BY TERRESTRIAL Pb CONTAMINATION CORRECTIONS

By

Daniel M. Unruh

T-2414

A thesis submitted to the Faculty and the Board of Trustees of the Colorado School of Mines in partial fulfillment of the requirements for the degree of Master of Science (Geochemistry).

Golden, Colorado

Date 12-3-80

Signed: Daniel M. Unruh

Daniel M. Unruh Student

Approved: Thomas Wildeman

Thomas R. Wildeman Advisor

Golden, Colorado

Date 12/3/80

George H. Kennedy

George H. Kennedy Head of the Department of Chemistry and Geochemistry

ABSTRACT

U, Th, and Pb analyses of whole-rock and troilite or magnetic separates from nine L chondrites suggest that the excess radiogenic Pb and the large variations in Pb-Pb model ages commonly observed in chondritic meteorites are largely due to terrestrial Pb contamination induced prior to analyses. Using the Pb isotopic composition of the troilite to calculate the isotopic composition of the Pb contaminants, the whole-rock data have been corrected for terrestrial Pb contamination in these meteorites prior to analysis. The L5 and L6 chondrites corrected for terrestrial Pb contamination yield a 4553±8 m.y. age, which is interpreted as the equilibration age of the L5-6 chondrites. The accretion age of the L chondrite parent body as determined from contamination-corrected concordant ages of the L3-4 chondrites is 4560±30 m.y. This age is not distinguishable from the equilibration age, but the large uncertainty allows for the possibility that accretion may have preceded metamorphism by ~30 m.y. The determination of the accretion age is further complicated by the possibility that the initial Pb in these meteorites was slightly ^{207}Pb-rich (evolved) relative to Canon Diablo troilite Pb.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

ACKNOWLEDGEMENTS

I am deeply indebted to Dr. M. Tatsumoto, U.S. Geological Survey, for providing analytical facilities, and for numerous useful comments which considerably improved this manuscript. I also thank Tom Wildeman, my thesis advisor, for his patience and help. Drs. E. C. Simmons and S. B. Romberger kindly served on my thesis committee and provided valuable comments.

The following individuals generously supplied the samples analyzed: E. Olsen, Chicago Field Museum (Bjurbolë); R. S. Clarke, U.S. National Museum of Natural History (Harleton, Mezö-Madaras, and Modoc); R. E. Folinsbee, University of Alberta (Bruderheim); J. O. Annexstead, NASA (AH77278); and R. Hutchison, British Museum (Natural History) (Barwell, Bishunpur, and Knyahinya). I also thank Dr. Hutchison for useful comments regarding sample selection and availability.

Finally, I wish to thank Ken Ludwig for the use of his plotting/regression program, Ed Daugs and Phil Heidt for laboratory maintenance and assistance, April Vuletich for assistance with mass spectrometry, and Marge Henneck and Karen Fenicle for typing the manuscript.

1. INTRODUCTION

There are two major problems regarding the U-Th-Pb systematics of chondritic meteorites. First, large apparent $^{207}Pb/^{206}Pb$ age differences (up to ~50m.y.) have been observed, even among chondrites of the same class and petrologic grade [1-5]. Second, most chondrites appear to have more ^{206}Pb, ^{207}Pb and ^{208}Pb than could have been derived from U and Th decay over the last ~ 4.55 b.y. (10^9y)[1-2, 5-6]. That is, when the data are plotted on a U-Pb evolution (concordia) diagram, assuming the Pb isotopic composition of Cañon Diablo troilite [2] as primordial, the data plot above the concordia curve. Three general interpretations (or combinations thereof) have been proposed to account for the apparent excess radiogenic Pb and apparent age differences: (1) complex (2 or more stages) U-Pb evolutionary histories, (2) variable primordial (initial) Pb isotopic compositions, and (3) terrestrial Pb contamination in excess of that accounted for by analytical Pb blanks [1-5].

The Pb-Pb model age differences may reflect real age differences, corresponding either to primary differences in the times of formation of the meteorite parent bodies or to either partial or complete resetting of the U-Pb clock

during later thermal or impact metamorphism [e.g. 2,5]. Evidence for recent disturbances to the Rb-Sr and K-Ar systems has been well-documented. Many shocked L chondrites show moderate to large amounts of radiogenic ^{40}Ar loss at ~300-500 m.y. ago [7-9]. These young ages are attributed to a major impact event (or events) and perhaps to the catastrophic break-up of the L-group parent body. Rb-Sr studies of shocked L-group chondrites [e.g. 10-11] also indicate that these meteorites have experienced metamorphism within the last 10^9 y.

Although periods of impact or thermal metamorphism on the chondrite parent bodies could conceivably explain the variations in Pb-Pb model ages, such an interpretation will not easily explain the apparent net enrichment of radiogenic Pb relative to U observed in most chondrites. In other words, a redistribution of U and Pb during metamorphism should not produce a net excess of Pb. In fact, because Pb is a fairly volatile element, one might expect any open-system behavior to produce Pb loss [e.g. 12,13]. Therefore, before any strict significance can be attached to the Pb-Pb model ages, the isotopic character of the non-radiogenic Pb must be evaluated.

The apparent ^{207}Pb-^{206}Pb model age differences and excess radiogenic Pb could result from the wrong choice for

the initial or primordial Pb isotopic composition [1,4,14-16]. There are, however, several good arguments against such an interpretation. First, there is at least 1 meteorite from each of the ordinary chondrite groups which is compatible with a Cañon Diablo troilite-type initial Pb. Second, the initial $^{206}Pb/^{204}Pb$ ratios in the meteorite parent bodies would have had to vary by a factor of 2 or more to account for the discordancy of some meteorite U-Pb data. Furthermore, because $^{207}Pb/^{206}Pb$ model ages show variations of up to 50 m.y. even within a single chondrite group and petrologic grade [1-4], the heterogenieties in initial Pb must have been present on a very small scale. Due to the volatility and geochemical incompatability of Pb in most meteoritic minerals it would seem improbable that large heterogenieties, even if initially present, could have been preserved during the thermal metamorphism which presumably produced the equilibrated chondrites [e.g. 17, and references therein].

The possibility of pre-analysis terrestrial Pb contamination has been acknowledged in virtually all U-Pb studies of meteorites. Manhes and Allegrè [5] have taken the view that all of the excess radiogenic Pb in chondrites is terrestrial. However, detailed studies of individual meteorites [18-20] have shown that terrestrial Pb

contamination alone would not account for the discordancy of some meteorite data, but the possibility of some terrestrial contamination could not be ruled out.

This work represents an attempt to determine the isotopic composition and source of the non-radiogenic Pb component in several L chondrites by studying the U-Th-Pb systematics of troilite separates and whole-rock splits from these meteorites. Troilite in iron meteorites may contain several ppm Pb but virtually no U [e.g. 2,21]. The only reported U-Pb analyses of chondritic troilite are those for the Barwell L5-6 [18] and Richardton H5 [22] chondrites. The troilite in these meteorites contained small amounts of U ($\leq$ 1ppb), but variable amounts of Pb (~20-300ppb). Consequently, barring Pb addition from an outside source, the Pb isotopic composition measured today should be little changed from that at the time the parent body formed. Therefore, troilite is probably the most likely phase from which to determine the isotopic character of the non-radiogenic Pb component.

2. EXPERIMENTAL PROCEDURES

2.1 Samples and Sample Preparation

In order to more fully evaluate the effects of sample handling, storage, and weathering on terrestrial Pb

contamination, samples subjected to a wide variety of pre-analysis conditions were chosen. The sample conditions and terrestrial residence times of the meteorites analyzed are summarized in Table 1. AH77278 is a "find", but does not appear to be badly weathered. All of the other meteorites analyzed were observed falls with terrestrial residence times ranging from 129y (Mezö-Madaras) to 15y (Barwell).

Samples used for whole-rock analyses consisted of ~50-100mg-sized chips taken from the interiors of pieces either sawn or broken from larger masses. In order to further minimize the potential effects of weathering and/or terrestrial contamination, chips were selected to be as free as possible from oxidation. However, traces of iron-staining (generally confined to the metallic phases) were present in virtually all samples. This procedure may produce a sampling bias toward metal depleted "whole-rock" analyses. Thus, the U, Th, and Pb abundances reported here may be somewhat higher than those in a truly representative sample.

The chips selected were washed for ~10 min in doubly-distilled 95% ethanol in an ultrasonic bath and dried at room temperature in a clean-air work station. The chips were then crushed to finer than ~ 0.3 mm in a stainless steel mortar. Disposable stainless steel inserts were used

TABLE 1. Sample conditions and terrestrial residence times of meteorites analyzed

Meteorite [1]	Res. Time [1]	Sampling [2]	Shock Facies [3]	Remarks
Bishunpur L3*	85y	2	--	Crusted stone, alteration confined to outer 1-2 mm
AH77278 L3**	find	3	--	Uncrusted but some exterior material; patchy alteration
Mezö-Madaras L3	128y	4	--	some iron-staining of silicate grains
Bjurböle L4	81y	1,2?	a	Fell through sea ice, very friable
Knyahinya L5	114y	1	d	Alteration confined to metal and occasionally to adjacent silicate grains
Barwell L5-6	15y	1	--	do.
Bruderheim L6	20y	1	d	do.
Harleton L6	19y	4	--	Contains troilite-rich veins, least-altered of all meteorites analyzed.
Modoc L6	75y	1 (2?)	b	somewhat more iron-stained than other chondrites

[1] Residence time and classification
From Hey [23] and Hutchison et al. [24]

[2]
1. chipped from the interior of an unsawn crusted stone
2. chipped from sawn stone several cm from saw cut
3. chipped <1-2 cm from saw cut
4. interior of a sawn cube. samples >1cm from sawn surfaces.

[3] Shock facies are from Dodd and Jarosewich [25]; shock effects increase from a→f.

*Recently reclassified LL3 by Dodd and Jarosewich [26].

**Tentative classification [27].

in the mortar to minimize cross-contamination. The alcohol-washing solutions were occasionally analyzed, and no evidence for preferential leaching of U, Th, or Pb from the samples was found, although some Pb with terrestrial isotopic ratios was removed by the washing procedure.

Troilite separates were generally obtained from partially crushed material by hand-picking under a microscope on a clean-air bench. Troilite in the Mezö-Madaras and Bishunpur chondrites was too fine-grained to be hand-picked. Consequently, a magnetic fraction (metal-matrix- and troilite-rich) was used in an attempt to find the least-radiogenic Pb in these chondrites. The troilite separate from Modoc was obtained using heavy liquids and an electro-magnetic separator. The troilite separates appeared to be >95% free from inclusions of other minerals.

2.2 Analytical Procedures

Wet-chemical procedures used in this study were similar to those given by Unruh et al. [18]. U, Th, and Pb concentrations were obtained using a ^{205}Pb-^{235}U-^{230}Th-enriched tracer during the early phase of this study and a ^{205}Pb-^{233}U-^{236}U-^{230}Th-enriched tracer in the later phase. The latter tracer enables us to determine not only the U, Th, and Pb abundances, but the fractionation-corrected U

isotopic compositions as well. The new tracer is quite pure ($^{238}U/^{233}U$ ~1.4×10^{-4}; $^{232}Th/^{230}Th$~6.2×10^{-4}; $^{206}Pb/^{205}Pb$~4.1×10^{-4}) so that spike-corrections to the isotopic composition data were generally insignificant.

Silicate samples were decomposed using either an HF-HNO_3 mixture in a teflon bomb at ~120°C for 3 days, or an HF-HNO_3-$HClO_4$ mixture at ~180° for 1 day. The latter procedure was used to ensure equilibration of Th between the sample and spike, but this procedure produced higher Pb blanks and was eventually discarded (see Table 2). Troilite samples were decomposed in a teflon beaker with 2N HBr.

Pb was separated from other elements using anion exchange in 0.5N HBr medium. A two-column procedure was employed. The semi-pure Pb fraction obtained from a 200ul column was loaded onto a 30ul column for final purification. When the sample size was 20mg the large column was not used and the small column was used twice. Pb blanks were generally 0.2-0.3ng (10^{-9}g) for whole-rock analyses and 0.1-0.2ng for troilite analyses. There were 2 exceptions in which ~0.5ng blanks were obtained (see Table 2). One of the higher blanks was traced to a contaminated HF-source and the other to the high-temperature HF-HNO_3-$HClO_4$ dissolution procedure (see footnotes, Table 2). Blank uncertainties were obtained from duplicate or triplicate

blank analyses performed concurrently with 1 to 4 sample analyses.

U and Th were separated together from other elements using anion exchange in 6.5N HNO_3 medium. U and Th blanks were 1-5pg (10^{-12}g) and 2-10pg, respectively. However, as pointed out in other studies [18,28], Th-contaminated filaments used for mass spectrometry can easily produce erroneous Th values in low-Th samples.

Isotopic ratios were obtained using an NBS-type, two-stage mass spectrometer. Pb was run using the single-filament, H_3PO_4-silica gel method, and U and Th were run by the conventional triple-filament technique. Data were obtained either by pulse-counting or from a Faraday cage and vibrating reed electrometer, depending upon the intensity of the ion beam. For more complete details, see Tatsumoto and Unruh [29].

Uncertainties in the reduced data (Tables 2-6) were obtained from equations equivalent to those given by Ludwig [30].

3. RESULTS

3.1 U, Th, and Pb Abundances

U, Th, and Pb abundances in nine L chondrites are shown in Table 2. Included are data from our previous study

of the Barwell L5-6 chondrite [18]. U and Th concentrations range from 5.5 to 15.0 ppb and 32.7 to 46.5 ppb, respectively. $^{232}Th/^{238}U$ ratios range from 2.7 to 6.2. The U concentrations, and consequently the Th/U ratios, show the greatest variation among the L6 chondrites. As previously pointed out in the experimental portion of this paper, some high Th values could reflect contamination. However, the high Th/U ratios for Barwell [18] and Harleton were reproducible to within a few percent. The data exhibit a crude trend of decreasing Th/U with increasing U and Th abundances, thus suggesting the presence of a high U, low Th/U component in these samples. Uranium is known to be heterogeneously distributed in chondrites and concentrated in minor phases such as chlorapatite and whitlockite [e.g. 31].

Both total Pb and ^{204}Pb abundances are shown in Table 2. The ^{204}Pb contents are more indicative of the true (primary) variations because the other Pb isotopes are comprised of both primordial Pb and radiogenic Pb from U or Th radioactive decay. ^{204}Pb abundances, and consequently the $^{238}U/^{204}Pb$ ratios, vary by more than 3 orders of magnitude. Furthermore, there is an overall trend of decreasing ^{204}Pb abundance from type 3 to types 5 and 6. However, within the L3 chondrites there is a 15-fold

Table 2. U, Th, and Pb Abundances and U Isotopic Compositions in Selected L-chondrites

Meteorite	Class	Sample Wt(mg)	Pb Blank [1] (ng)	ppb U	ppb Th	ppb Pb	ppb ^{204}Pb	Atomic Ratios $^{238}U/^{204}Pb$	Atomic Ratios $^{238}U/^{235}U$	Atomic Ratios $^{232}Th/^{238}$
Bishunpur	L(LL)3	82.75	0.35±.07	11.70±.08	37.7±2.4	366 ±2	6.66 ±.04	1.49 ±.01	137.7± .4	3.34±.22
AH77278 [2]	L3	64.94	0.53±.12	12.16±.19	46.5± .4	1014 ±11	19.1 ±.2	0.542 ±.010	--	3.95±.07
		52.64	0.24±.05	9.24±.08	25.5± .2	1091 ±7	20.8 ±.1	0.377 ±.004	137.1±0.7	2.85±.03
Mezö-Madaras	L3	56.49	0.53±.12	11.66±.09	38.7± .4	5451 ±25	106.3 ±.5	0.0933±.0008	--	3.43±.03
		73.03	--	11.67±.07	39.0± .2	--	--	--	137.5± .8	3.45±.03
Bjurböle	L4	61.99	0.30±.06	11.50±.06	41.7± .3	134.5 ± 1.0	2.01 ±.02	4.88 ±.05	--	3.75±.04
Knyahinya	L5	61.04	0.53±.10	13.11±.09	43.7±1.0	35.4 ± .7	0.081±.014	137 ±25	--	3.44±.08
		71.09	0.22±.03	13.74±.09	45.8± .4	38.4 ± .2	0.120±.004	97.6 ±3.5	137.4 ±1.0	3.45±.04
Barwell [3]	L5-6	100.19	0.27±.08	9.35±.07	38.9± .5	33.8 ± .4	0.149±.007	53.2 ±2.6	137.2 ± .6	4.30±.07
		93.40	0.27±.08	9.84±.05	--	39.0 ± .4	0.230±.007	38.8 ±1.2	--	--
Bruderheim	L6	107.26	0.30±.06	13.93±.07	36.6± .9	46.2 ± .4	0.238±.006	49.8 ±1.3	--	2.71±.06
		89.50	0.22±.03	14.98±.09	44.9± .3	44.3 ± .2	0.205±.003	63.0 ±1.1	137.6 ± .8	3.10±.03
Harleton	L6	95.98	0.30±.06	6.22±.04	37.5± .2	48.1 ± .4	0.422±.006	12.53 ± .18	--	6.23±.05
		75.29	0.22±.03	5.51±.03	32.8± .3	33.3 ± .2	0.263±.003	17.78 ± .24	137.3 ±1.2	6.12±.06
Modoc	L6	63.55	0.53±.10	12.59±.08	42.9±3.5	64.8 ± .8	0.514±.012	20.83 ± .51	137.5 ± .8	3.53±.28
		92.35	0.22±.03	14.61±.08	48.5± .9	70.1 ± .3	0.518±.004	23.98 ± .22	137.3 ± .6	3.43±.06

[1] Blank uncertainties are calculated from the reproducibility of duplicate or triplicate blank analyses with a given set of samples. The high blanks for Bishunpur-Mezö-Madaras, and Modoc-Knyahinya were the result of high temperature bomb dissolution with perchloric acid, and a contaminated HF source, respectively.

[2] Classification tentative [27].

[3] Data are from [18] except the $^{238}U/^{235}U$ ratio which is from this work.

variation in the ^{204}Pb concentrations. The magnitude and trend of the ^{204}Pb variations are consistent with those seen in other heavy volatiles, Tl and Bi [32-34], and in the noble gases [e.g. 35]. Hg is the only heavy volatile which does not appear to follow the trend [6,36].

The rather surprising aspect of the Pb data is the apparent increase in ^{204}Pb from petrologic type 5 to type 6. However, in view of possible terrestrial Pb contamination of these meteorites, the apparent reversal of the trend may not be real. The terrestrial Pb problem will be discussed in detail in Section 4.

Uranium isotopic compositions were found to be, within error, the same as the terrestrial value of $^{238}U/^{235}U=137.9$, thus confirming the observations of Chen and Wasserburg [37]. The somewhat lower $^{238}U/^{235}U$ ratio (135.2±.2) which was originally measured in Barwell [18] was found to be in error. The error presumably resulted either from ^{235}U contamination from a previously used isotopic tracer or to background contributions to the ^{235}U peak during mass spectrometry. In any case, the complete rebuilding of the vacuum pumping system in the mass spectrometer, and total elimination of the ^{235}U tracer from the laboratory seem to have eliminated the problem.

3.2 Pb isotopic compositions and U-Pb systematics

The Pb isotopic compositions of the bulk chondrites are shown in Table 3. As one might expect from the U and Pb abundances, Pb in the L3 chondrites is very non-radiogenic ($^{206}Pb/^{204}Pb \sim 9.4$-$11.0$) whereas that in the L5-L6 chondrites is moderately to very radiogenic ($^{206}Pb/^{204}Pb \sim 30$-$160$). The Pb isotopic characters of the individual meteorites are reasonably reproducible, considering that analyses were performed on separate chips rather than powder splits.

The Pb isotopic data are plotted on a $^{207}Pb/^{204}Pb$ vs. $^{206}Pb/^{204}Pb$ diagram in Figure 1. The data define a linear array, the slope of which corresponds to an age of 4528±9 m.y. (2σ, [38]). The error includes the scatter of the points about the best-fit line. As one can see from the large value of $S/(N-2) \sim 20$ (S= Sums of the squares of the residuals; N= No. of samples, [38]), the data are quite badly scattered. Thus, the apparent 4528 m.y. age is of questionable significance.

The U-Pb data are plotted on a U-Pb concordia diagram [39] in Figure 2. The trend defined by the data intersects the concordia curve at 4544±17 m.y. and -395±385 m.y. The data are corrected for the Pb isotopic composition of Cañon Diablo troilite Pb [2] as the assumed initial Pb isotopic composition. The large uncertainties for Mezö-Madaras and

Table 3. Pb Isotopic Compositions and Pb-Pb Model Ages

of selected L chondrites

		RAW DATA			CORRECTED FOR BLANK AND MASS FRACTIONATION [1]				
Meteorite	Class	$^{206}Pb/^{204}Pb$	$^{207}Pb/^{206}Pb$	$^{208}Pb/^{206}Pb$	$^{206}Pb/^{204}Pb$	$^{207}Pb/^{206}Pb$	$^{208}Pb/^{206}Pb$	ρ [2]	$^{207}Pb/^{206}Pb$ [3] model age (m.y.)
Bishunpur	L(LL)3	10.999±.013	1.0284±.0008	2.800±.0038	10.298±.015	1.0336±.0009	2.821±.004	0.839	4550±14
AH77278	L3	10.224±.030	1.0574±.0010	2.945±.005	10.196±.032	1.0609±.0012	2.960±.006	0.944	4477±50
		9.947±.010	1.0707±.0007	2.996±.006	9.940±.012	1.0732±.0008	3.007±.006	0.859	4486±36
Mezö-Madaras	L3	9.437±.009	1.0971±.0006	3.127±.002	9.446±.011	1.0989±.0006	3.136±.002	0.899	4550±125
Bjurböle	L4	15.673±.040	0.9062±.0022	2.246±.003	15.615±.045	0.9098±.0023	2.254±.003	0.742	4556±13
Knyahinya	L5	78.6 ±.8	0.6709±.0010	1.141±.004	161 ± 19	0.6469±.0048	0.997±.025	0.998	4553±5
		92.5 ±1.6	0.6645±.0007	1.108±.002	115.9 ±4.1	0.6570±.0014	1.063±.007	0.999	4553±3
Barwell [4]	L5-6	63.4 ±.2	0.6862±.0013	1.337±.004	74.8 ±3.3	0.6779±.0027	1.297±.012	0.996	4549±4
		50.8 ±.2	0.7028±.0010	1.309±.002	56.7 ±1.6	0.6961±.0022	1.270±.010	.994	4545±3
Bruderheim	L6	61.7 ±.4	0.6847±.0012	1.135±.006	68.6 ±1.5	0.6791±.0019	1.099±.010	0.992	4537±4
		70.3 ±.1	0.6725±.0003	1.077±.002	78.8 ±1.2	0.6674±.0009	1.042±.996	0.996	4529±1
Harleton	L6	29.7 ±.1	0.7543±.0010	1.867±.008	30.8 ±1.2	0.7519±.0019	1.859±.010	0.947	4504±5
		29.38 ±.06	0.7584±.0008	1.888±.001	30.5 ± .1	0.7550±.0011	1.883±.002	0.948	4510±4
Modoc	L6	35.4 ±.3	0.7378±.0012	1.488±.003	38.9 ± .3	0.7298±.0020	1.437±.005	0.952	4535±6
		41.6 ±.2	0.7177±.0015	1.380±.004	42.9 ± .3	0.7158±.0020	1.367±.005	0.904	4527±5

[1] Blank uncertainties from Table 2; Isotopic compositions: $\alpha = 19.0 \pm .1$, $\beta = 15.65 \pm .05$, $\alpha = 38.5 \pm .3$; mass fractionation correction was 0.1 ±.03%/mass unit.

[2] Correlation coefficient between $^{206}Pb/^{204}Pb$ and $^{207}Pb/^{204}Pb$.

[3] Model ages relative to Cañon Diablo Troilite Pb [2].

[4] Data from [18].

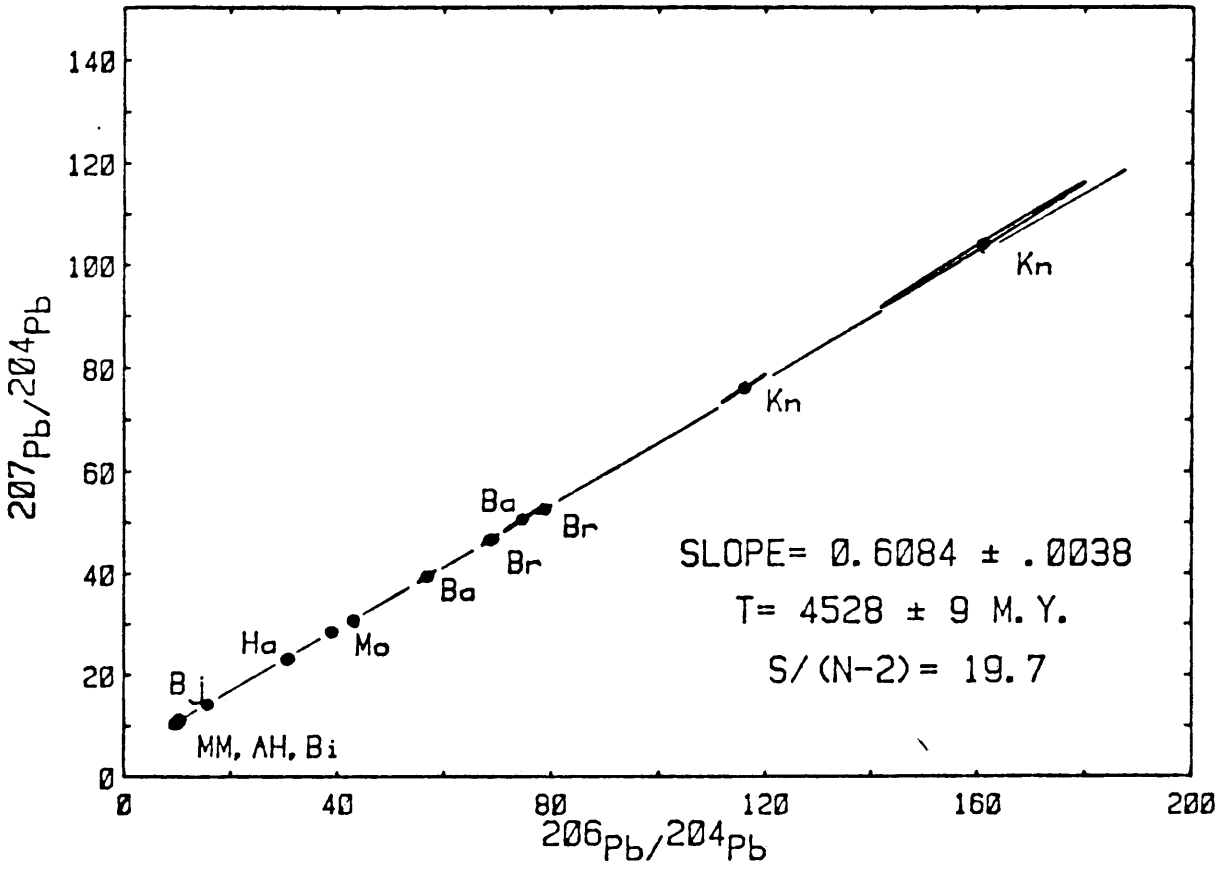

Figure 1. $^{207}Pb/^{204}Pb$ vs. $^{206}Pb/^{204}Pb$ diagram for L chondrites. The best-fit line yields a 4528±9 m.y. age. Uncertainties are 2σ(a priori) x $\sqrt{S/(N-2)}$[38]. Abbreviations used are MM=Mezö-Madaras, AH=AH77278, Bi=Bishunpur, Bj=Bjurböle, Kn=Knyahinya, Ba=Barwell, Br=Bruderheim, Ha=Harleton, Mo=Modoc.

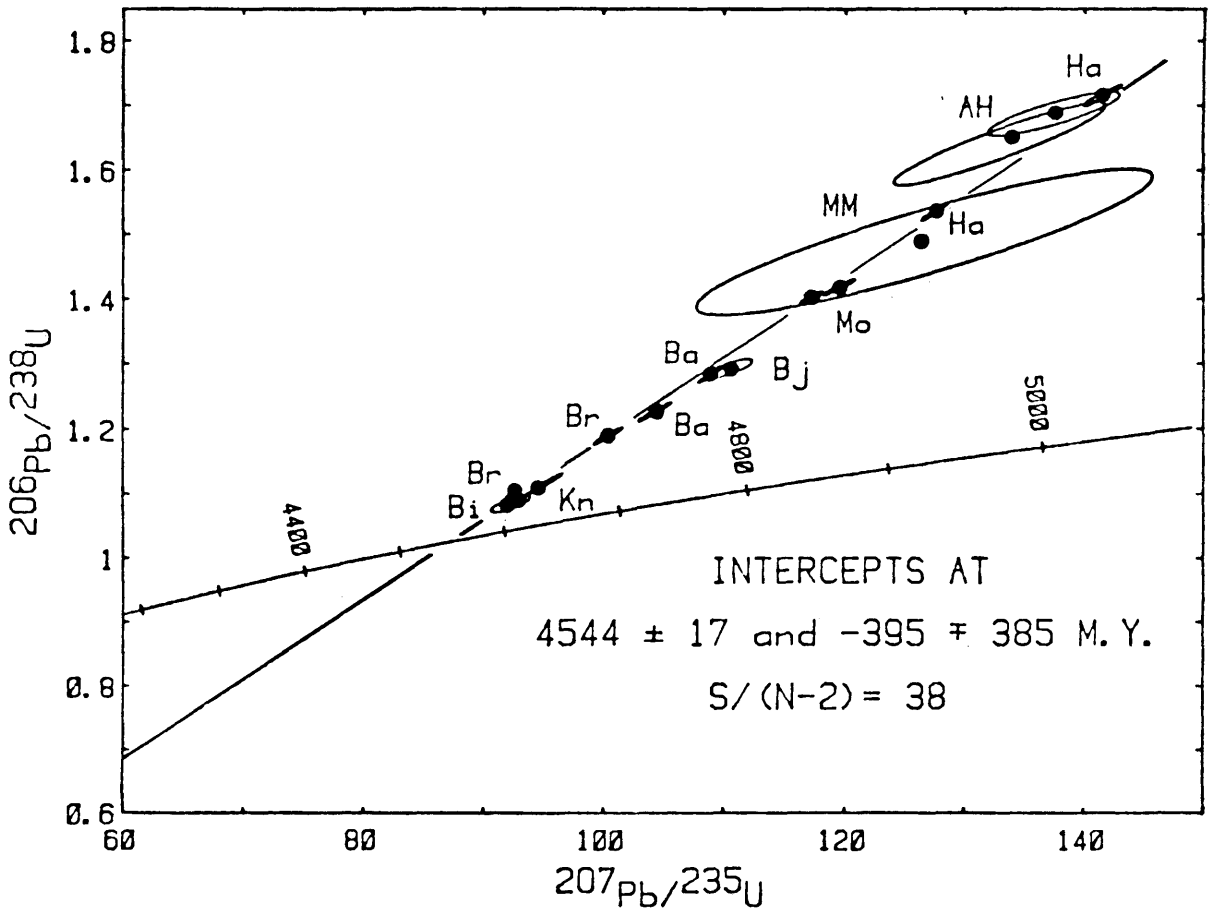

Figure 2. U-Pb concordia diagram for L chondrites. The best-fit line intersects the concordia curve at 4544±17 and -395±385 m.y. The data are corrected for Cañon Diablo troilite Pb as the initial Pb isotopic composition [2]. The younger intercept lies off the diagram to the lower left.

AH77278 result from propagation of errors due to the large initial Pb correction (~99% and 95%, respectively). Data for the L5-L6 chondrites alone yield 4540±20 m.y. and -356±475 m.y. intercepts. The upper intercept is in fair agreement with the Pb-Pb age (Fig. 1) and a recent disturbance to the U-Pb system is suggested by the near-0 m.y. lower intercept.

There are two factors which preclude such a simple interpretation. First, all of the data plot above the concordia curve, showing from ~5 to 70% excess radiogenic Pb. If the ~0 m.y. event caused large-scale Pb redistribution on the parent body, then one would expect the data either to be linearly distributed about the condordia curve or to plot below the curve as a result of recent Pb loss [e.g. 12,13,40]. Second, the data are grossly scattered with S/(N-2)=38 for all data and 69 for the L5-L6 chondrites alone. A two-stage model such as the one discussed in detail by Gale et al. [20] would predict a precise linear array on the concordia curve (S/(N-2) ~ 1), provided that the data are corrected for the proper initial Pb isotopic composition. Therefore, these meteorites were either formed, metamorphosed, or shocked at distinctly different times; or variable amounts of Pb, isotopically distinct from that in Cañon Diablo troilite, has been added

at some time during the meteorites' histories. It is this latter possibility that we have chosen to investigate in detail ([18], and this work).

In a rigorous sense, it is not possible to determine whether Pb was added at the time of formation of the meteorite parent body, in the form of variable initial Pb isotopic compositions grossly enriched in the radiogenic Pb isotopes relative to Cañon Diablo troilite Pb, or very recently via terrestrial contamination. However, by measuring the isotopic composition of the non-radiogenic Pb component, the apparent initial Pb, it may be possible to infer the source of the excess Pb from this isotopic composition.

3.3 U-Th-Pb analyses of troilite and magnetic separates.

In order to further examine the excess radiogenic Pb problem, troilite or magnetic separates have also been analyzed in hope of finding the least-radiogenic-Pb component in these meteorites. The U, Th, and Pb concentrations of these separates are shown in Table 4 and the Pb isotopic compositions in Table 5.

U and Th concentrations of the troilite separates, though variable and lower than those in the whole-rock, are generally higher than expected. These abundances and the

Table 4. U, Th, and Pb Abundances in Troilite and Magnetic Separates from L Chondrites

Sample	Class	Sample Wt (mg)	Pb Blank (ng)	ppb			Atomic Ratios	
				U	Th	Pb	$^{232}Th/^{238}U$	$^{238}U/^{204}Pb$
TROILITE SEPARATES								
AH77278	L3	11.70	0.121 ± .008	0.14 ± .07	0.18 ± .07	28.4 ± .8	1.3 ± .8	0.25 ± .12
Bjurböle	L4	15.90	0.121 ± .008	0.65 ± .07	1.00 ± .05	55.9 ± .5	1.59± .19	0.67 ± .07
Knyahinhya	L5	10.34	0.095 ± .014	0.30 ± .06	0.41 ± .21	6.5 ± .7	1.4 ± .8	3.0 ± .5
Barwell [1]	L5-6	17.93	0.30 ± .06	0.85 ± .07	0.65 ± .05	199 ± 3	0.80± .09	0.27 ± .02
Bruderheim	L6	10.46	0.20 ± .02	1.47 ± .09	1.58 ± .18	43.6 ±1.7	1.11± .14	2.24 ± .17
Harleton	L6	5.15	0.20 ± .02	2.30 ± .34	2.44 ± .52	150 ± 3	1.09± .29	1.00 ± .15
Modoc	L6	33.59	0.095 ± .014	0.99 ± .02	1.32 ± .04	106 ± 1	1.38± .05	0.60 ± .02
MAGNETIC SEPARATES								
Bishunpur	L(LL)3	20.69	0.28 ± .02	7.03 ± .08	17.4 ± .2	525 ± 2	2.55± .04	0.605± .007
Mezö-Madaras	L3	25.99	0.28 ± .02	2.77 ± .05	8.68 ± .2	7283 ± 17	3.23± .09	0.0165± .0003

[1] Tr 2 from Table 2 of [18].

Table 5. Blank-corrected and Apparent Initial Pb Isotopic Compositions in Troilite and Magnetic Separates from L Chondrites

Sample	Type	Corrected for Blank and Mass Fractionation				Apparent Initial Pb Isotopic Compositions [1]			
		$^{206}Pb/^{204}Pb$	$^{207}Pb/^{204}Pb$	$^{208}Pb/^{204}Pb$	ρ	$^{206}Pb/^{204}Pb$	$^{207}Pb/^{204}Pb$	$^{208}Pb/^{204}Pb$	ρ
TROILITE SEPARATES									
AH77278	L3	12.41 ± .10	12.07 ± .11	32.47 ± .32	0.849	12.15 ± .15	11.91 ± .13	32.39 ± .33	0.877
Bjurböle	L4	16.90 ± .04	14.63 ± .04	36.74 ± .12	0.739	16.19 ± .09	14.18 ± .07	36.46 ± .12	0.874
Knyahinya	L5	19.30 ± .28	16.35 ± .34	38.45 ± .80	0.707	16.35 ± .35	14.45 ± .48	37.38 ± .97	0.856
Barwell[2]	L5-6	18.44 ± .05	15.67 ± .05	37.85 ± .12	0.910	18.16 ± .06	15.49 ± .05	37.79 ± .12	0.940
Bruderheim	L6	19.84 ± .16	16.47 ± .18	39.50 ± .52	0.733	17.55 ± .24	15.04 ± .21	38.88 ± .52	0.896
Harleton	L6	19.24 ± .09	16.04 ± .11	39.02 ± .26	0.723	18.21 ± .18	15.41 ± .14	38.75 ± .26	0.850
Modoc	L6	18.94 ± .03	15.99 ± .05	38.73 ± .13	0.710	18.32 ± .03	15.61 ± .05	38.52 ± .13	0.715
MAGNETIC SEPARATES									
Bishunpur	L(LL)3	10.181± .017	10.845± .022	30.183± .064	0.833	9.561± .019	10.462± .023	29.793± .064	0.828
Mezo-Madaras	L3	9.352± .008	10.335± .010	29.550± .032	0.941	9.335± .008	10.324± .010	29.537± .032	0.941

[1] Calculated from the $^{238}U/^{204}Pb$ ratios (Table 4) and an assumed age of 4550 m.y.

[2] Tr2 from Table 3 of [18].

low Th/U ratios relative to the bulk meteorites probably reflect the presence of small amounts of mineral impurities enriched in U relative to Th. The higher U and Th abundances in the magnetic separates are the result of silicate-matrix being intergrown with the metal. Pb abundances are also quite variable and are not correlated with the Pb abundances in the whole-rocks. However, by comparing Figure 2 and Table 4 one can see that there is a crude correlation between the amount of excess radiogenic Pb in the whole-rocks and the Pb concentrations in the troilite.

Both the blank-corrected and U- and Th-decay-corrected (apparent initial) Pb isotopic compositions are shown in Table 5. The apparent initial Pb isotopic compositions are plotted on a $^{207}Pb/^{204}Pb$ vs. $^{206}Pb/^{204}Pb$ diagram in Figure 3. The terrestrial Pb field consists of reported blank isotopic compositions [3,5,18,19,28,41, and this work] in several U.S. and European cities. This field should represent the most probable range of isotopic compositions of industrial or pollutant Pb contaminants, but of course not all possible terrestrial Pb contaminants. Also shown for reference are Cañon Diablo troilite Pb (CD) and a 4550 m.y. reference line (solid line).

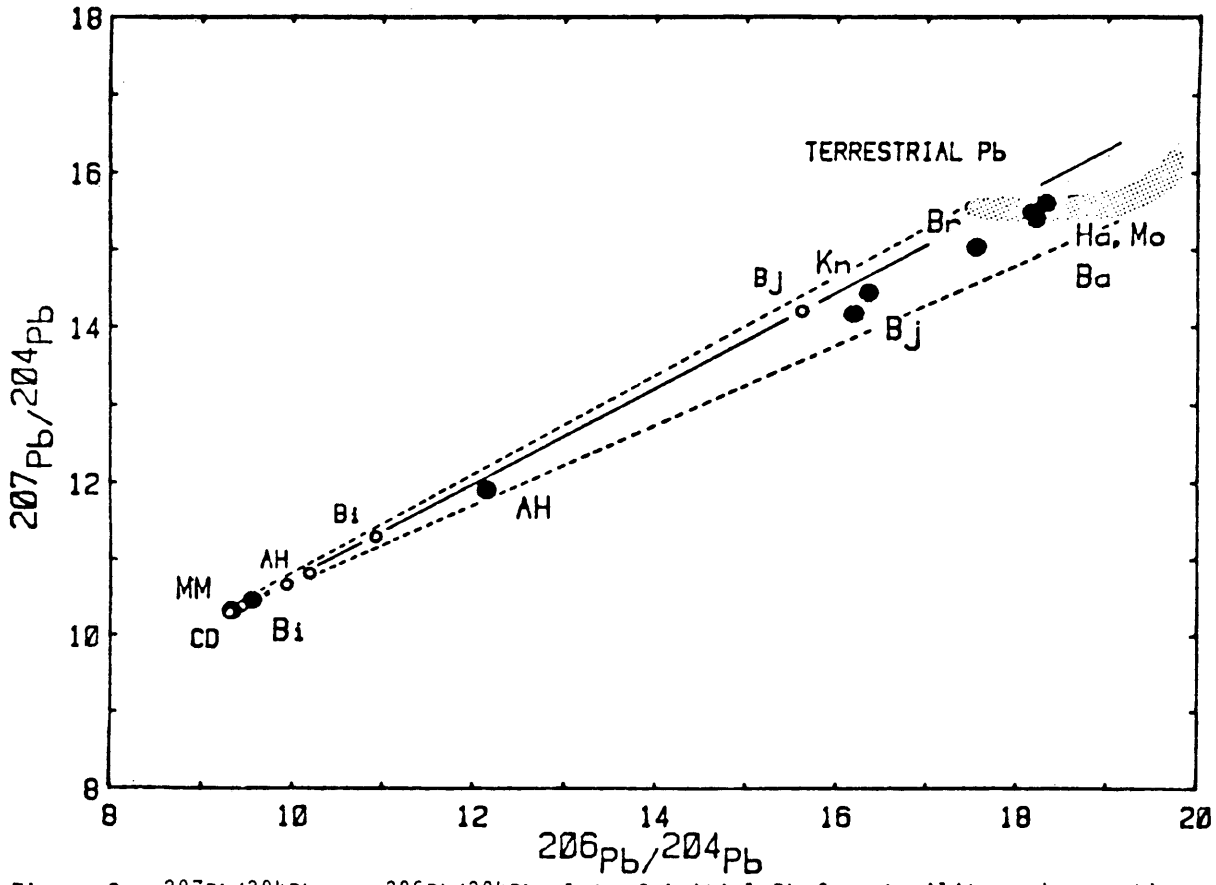

Figure 3. $^{207}Pb/^{204}Pb$ vs. $^{206}Pb/^{204}Pb$ plot of initial Pb from troilite and magnetic separates. Troilite and magnetic separates are shown by filled circles, and whole-rocks by smaller open circles. CD is Cañon Diablo troilite Pb. The stippled field shows the most probable isotopic compositions of contaminant Pb. Most of the data fall within the region of possible mixtures of Cañon Diablo Pb and terrestrial Pb (broken lines). The solid line is a 4550 m.y. reference line.

All of the troilite data plot within the area bounded by the terrestrial Pb field and Cañon Diablo troilite Pb (dashed lines). Furthermore, the data from those samples which are most discordant in the lead-excess direction in Fig. 2 and show the highest troilite Pb abundances, plot near or within the terrestrial field. The troilite Pb data plotted on a $^{208}Pb/^{204}Pb$ vs. $^{206}Pb/^{204}Pb$ diagram exhibit the same features. Consequently, the most likely interpretation is that the Pb in these separates, and therefore the excess Pb in the whole-rocks, is indeed terrestrial.

The interpretation of the magnetic separate data is not as straight forward. The Mezö-Madaras magnetic data lie distinctly outside the terrestrial Pb-Cañon Diablo troilite Pb envelope (Fig. 3) and, in fact, the high slope (~1.1) of the line connecting this sample and Cañon Diablo troilite Pb is not easily explained by any terrestrial Pb contaminant. The Bishunpur magnetic separate is also slightly ^{207}Pb-rich, although the data do not plot distinctly outside the terrestrial Pb-Cañon Diablo Pb field.

4. DISCUSSION

Once it has been established that these meteorites are contaminated with terrestrial Pb in excess of that accounted for by analytical blanks, then the amount and isotopic

composition of the contaminant must be determined before any rigorous significance can be attached to the apparent ages (Figs. 1 and 2). Two approaches to this problem have been employed. Both involve using the Pb isotopic compositions of the troilite separates to approximate the extent and nature of the Pb contaminant.

4.1 Terrestrial Pb corrections: Troilite "initial" Pb

Given that the terrestrial Pb contamination observed in the troilite separates indicates contamination of the bulk meteorites, then the proper non-radiogenic Pb correction to the whole-rock data will consist of a mixture of terrestrial Pb and true initial Pb. The range of possible corrections, then, is given by a mixing-line in Figure 3 through the chondrite troilite apparent initial Pb and Cañon Diablo troilite Pb, the assumed initial Pb. If the individual whole-rocks and troilite separates contain the same relative proportions of contaminant Pb and indigenous initial Pb, then use of the troilite apparent initial Pb isotopic compositions as the non-radiogenic Pb corrections to the whole-rocks is approximately valid. Clearly, this assumption will not hold for AH77278 and Bjurböle (Fig. 3), because the troilite compositions are more radiogenic than the whole-rocks. Therefore, correction for the troilite Pb would produce negative ages.

The troilite corrected data for the L5-L6 chondrites are plotted on a U-Pb concordia diagram in Figure 4. All of the data now plot within +3 to -12% of the concordia curve. The trend defined by the data intersects the concordia curve at 4553±8 m.y. and 367±586 m.y. The amount of scatter has been reduced by a factor of 6 relative to the Cañon Diablo-corrected data S/(N-2)~11 but there is still much more scatter than would be predicted by the assigned uncertainties. Therefore, the ages obtained will have real significance only if the scatter is normally distributed about the best-fit line--that is if the scatter results from random over- or under-correction of the individual samples for terrestrial Pb. Close examination of the data suggests that this indeed may be the case. Those meteorites, Harleton and Modoc, on which the troilite correction had the largest effect (~50% of the ^{206}Pb) show the largest deviations from the best-fit line. Furthermore, the mean value of the two analyses of each meteorite plot on or near the best-fit line. In any case, the near concordancy or "normal" discordancy exhibited by most of the data suggest that the 4553±8 m.y. age represents a better approximation of the true age than does the age obtained by correcting the data for Cañon Diablo troilite Pb alone. This age is in excellent agreement with the 4552 m.y. Pb-Pb model ages of

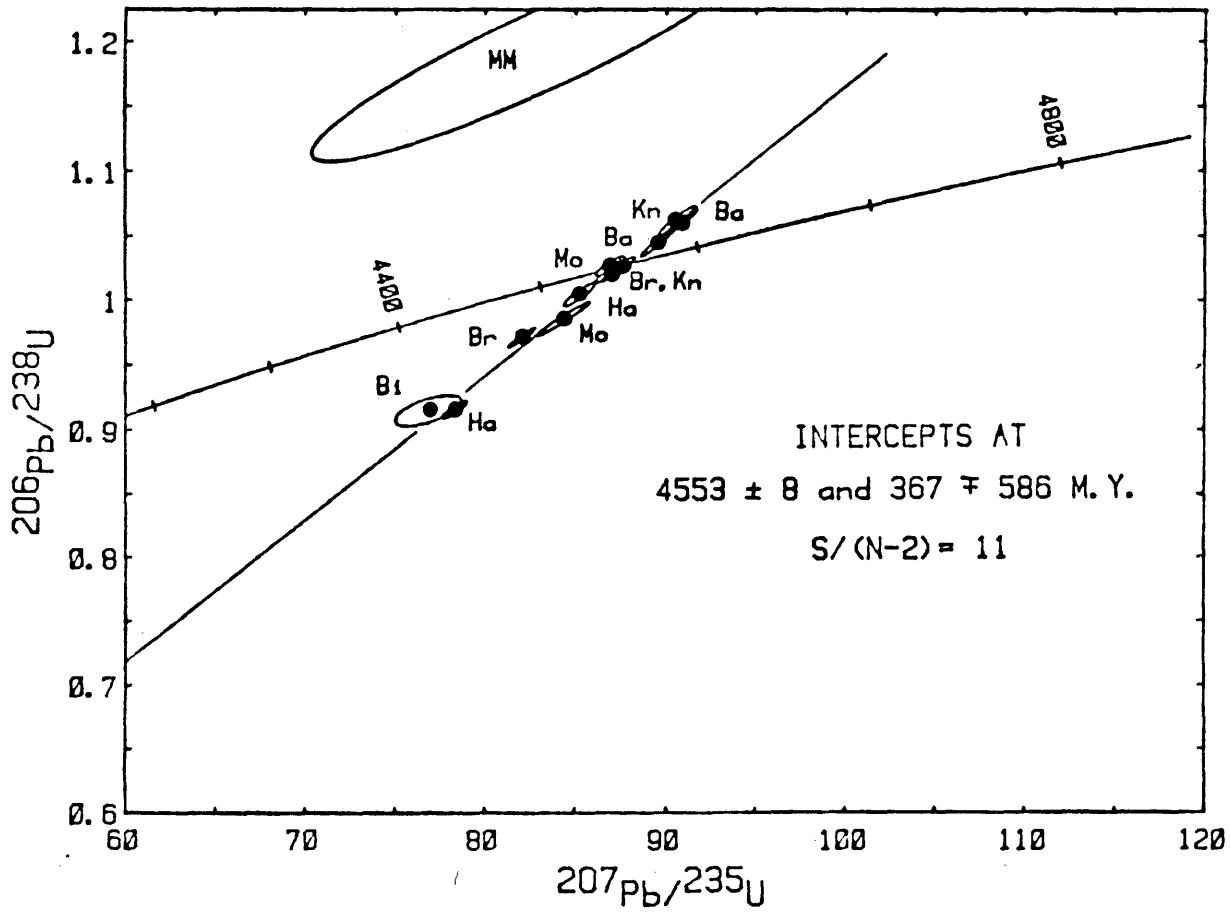

Figure 4. U-Pb concordia diagram for chondrite troilite-corrected data. The data from the L5-L6 chondrites define an array that intersects the concordia curve at 4554±8 m.y. and 367±586 m.y. Mezö-Madaras and Bishunpur data corrected for the apparent initial Pb in the magnetic separates are shown for reference.

two nearly-concordant L5 chondrites determined by Manhes and Allegre [5].

The 367±586 m.y. lower intercept, though imprecisely defined, is in accord with the ~500 m.y. disturbances to the K-Ar systems [7-9] and recent disturbances to the Rb-Sr system [10-11] observed in many shocked L chondrites. One should note, however, that because most of the data cluster around the upper intercept (Fig. 4), the lower intercept is very sensitive to any contamination-correction bias. Thus the apparent agreement may be fortuitous.

The magnetic-corrected data for Bishunpur and Mezö-Madaras are also shown in Fig. 4. The Bishunpur data plot, within uncertainty, on the L5-L6 chord whereas the Mezö-Madaras data, though very uncertain, do not. The significance of the Mezö-Madaras data in terms of possible real variations in the initial Pb isotopic composition will be discussed in section 4.5.

4.2 Terrestrial Pb corrections: Single-stage approximations.

The second approach to correction of the data for terrestrial Pb contamination involves the assumption of closed-system U-Pb evolution. That is, the U-Pb data are assumed to be precisely concordant, and all deviations from

concordancy in the Pb-excess direction are assumed to be solely the result of terrestrial Pb contamination.

These corrections require that the Pb isotopic composition of the contaminant be known. The contaminant Pb isotopic compositions have been calculated for each of the meteorites analyzed by assuming that the apparent initial Pb in the troilite (or magnetic) separates is a mixture of Cañon Diablo-type Pb and "normal" terrestrial Pb (the terrestrial Pb field in Fig. 3). The intersection of a line through Cañon Diablo and the troilite Pb with the best-fit line through the terrestrial Pb field ($^{207}Pb/^{204}Pb=0.0898 \times ^{206}Pb/^{204}Pb + 13.92$) yields the $^{206}Pb/^{204}Pb$ and $^{207}Pb/^{204}Pb$ ratios of the contaminant. The $^{208}Pb/^{204}Pb$ ratio is calculated from the $^{206}Pb/^{204}Pb$ ratio and the best-fit approximation to the terrestrial Pb field ($^{208}Pb/^{204}Pb = 0.697 \times ^{206}Pb/^{204}Pb + 25.3$). These equations can only be used in the range of $^{206}Pb/^{204}Pb$ ~16-19. Pb with the calculated isotopic composition is then used as a second blank correction such that the U-Pb data become concordant when Cañon Diablo troilite Pb is used as the initial Pb.

The calculated isotopic compositions of the Pb contaminants are shown in Table 6. The high $^{207}Pb/^{206}Pb$ apparent initial ratio for the Mezö-Madaras magnetic separate precludes a reasonable calculation of an isotopic

Table 6. Pb Contaminant Isotopic Compositions and Calculated Contaminant and Indigenous ^{204}Pb Abundances

Sample	Type	Terrestrial Contaminant Pb [1]			Contamination ^{204}Pb ppb [2]		Indigenous ^{204}Pb ppb [2]	
		$^{206}Pb/^{204}Pb$	$^{207}Pb/^{204}Pb$	$^{208}Pb/^{204}Pb$	Whole-rock	Troilite	Whole-rock	Troilite
AH77278	L3	18.6 ± .6	15.59 ± .06	38.3 ± .5	0.71,0.56	0.14	18.4 20.2	.34
Bjurböle	L4	18.7 ± .1	15.60 ± .01	38.3 ± .1	0.27	0.59	1.74	.20
Knyahinya	L5	18.1 ± .8	15.54 ± .08	37.9 ± .6	0.08, .09	0.07	∿0, 0.03	.02
Barwell	L5 [3]	18.3 ± .1	15.56 ± .01	38.1 ± .1	0.15,0.23	2.6	∿0, ∿0	.05
Bruderheim	L6	18.5 ± .3	15.58 ± .03	(38.2 ± .3)	0.21,0.11	0.51	0.03, 0.09	.05
Harleton	L6	18.5 ± .2	15.58 ± .02	(38.2 ± .2)	0.40,0.26	1.9	0.02, 0.06	.06
Modoc	L6	(18.2 ± .1)	(15.56 ± .01)	(38.0 ± .1)	0.46,0.52	1.4	0.05, ∿0	∿0
Bishunpur	L(LL)3	17.1 ± .9	15.46 ± .09	37.2 ± .6	0.08	--	6.6	--
Mezö-Madaras	L3 [4]	--	--	--	(0.52)	--	(106)	--

[1] Calculated from the intersection of a line through Cañon Diablo Troilite Pb and the apparent initial Pb isotopic composition of the Troilite (Table 5): ($^{207}Pb/^{204}Pb$=0.0898 x ($^{206}Pb/^{204}Pb$) + 13.92, ($^{208}Pb/^{204}Pb$) = 0.697 x ($^{206}Pb/^{204}Pb$) + 25.3. Values in parentheses are lower than the apparent initial ratios. In these instances the apparent initial ratios were used to calculate concordant model ages.

[2] Calculated concentrations assuming concordancy (Fig. 5). The concentration of total Pb contamination is ∿75 x the ^{204}Pb value. The total indigenous initial Pb concentration is ∿50 x the ^{204}Pb value.

[3] Data calculated from TR2 from Tables 2 and 3 of [18].

[4] The calculated contaminant Pb isotopic composition lies far outside the "normal" range. Contaminant and indigenous Pb values are calculated by assuming that contaminant has an average "normal" isotopic composition.

contaminant for this sample. The calculated values lie far outside the "normal" terrestrial field and outside the range of validity of the assumed terrestrial trends. In fact, if the deviation from Cañon Diablo troilite Pb is the result of terrestrial Pb contamination alone, then the contaminant would have to be Archean ore-type Pb. This interpretation is considered improbable. The calculated $^{208}Pb/^{204}Pb$ ratios of the contaminants in the three L6 chondrites (and the $^{206}Pb/^{204}Pb$ and $^{207}Pb/^{204}Pb$ ratios in Modoc) are slightly lower than the apparent initial ratios in the troilite--that is, the data plot slightly above the assumed terrestrial trend (c.f. Fig. 3). These ratios are shown in parentheses in Table 6. In these instances the apparent initial ratio in Table 4 was used as that of the contaminant.

The terrestrial-Pb-corrected concordant $^{207}Pb/^{206}Pb$ ages are shown in Figure 5. The mean age of the L5-L6 chondrites is 4551±5 m.y. (2σ) although the data are quite scattered ($S/(N-1)\sim16$). The age is nearly identical to the upper concordia intercept obtained by the previous correction procedure.

The maximum correction possible by this method is obtained by removal of all ^{204}Pb and proportionate amounts of the other isotopes as terrestrial contamination. Some of the samples (open circles in Fig. 5) still plot ~1-3% above

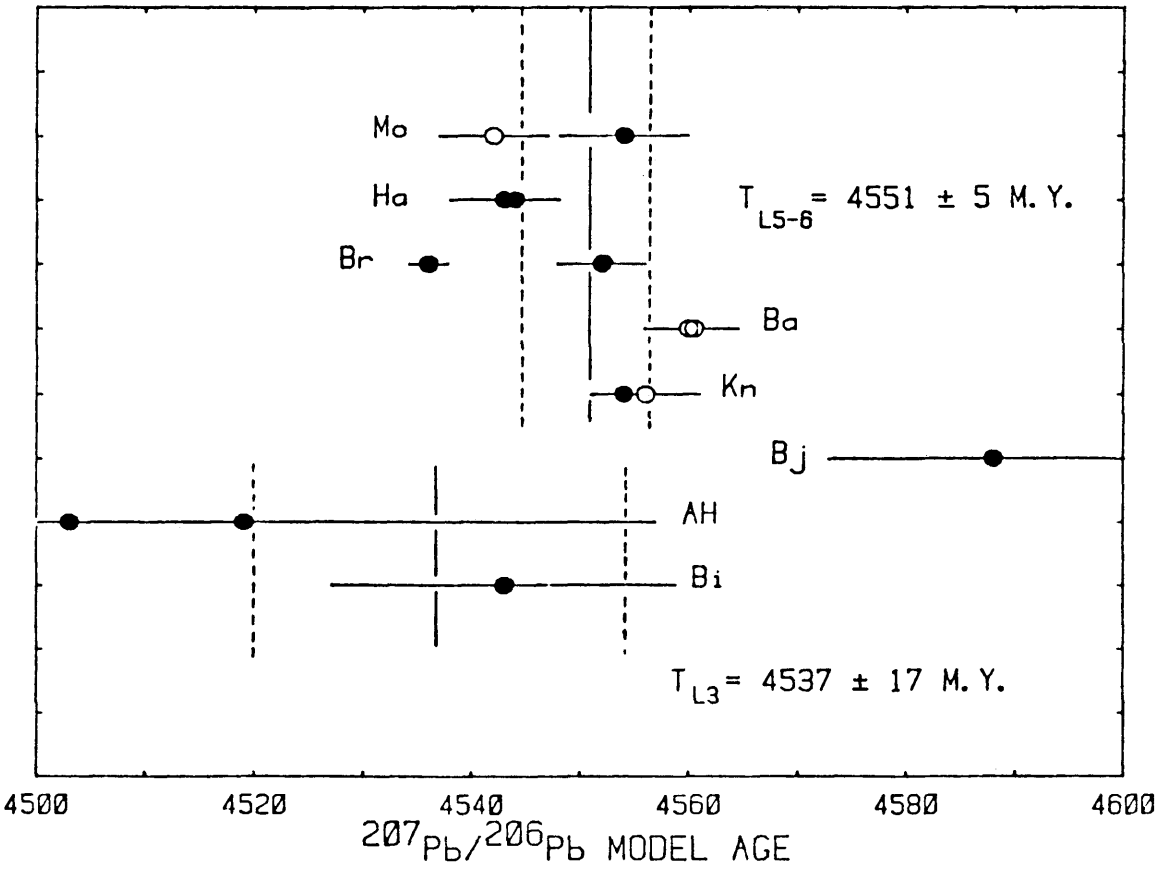

Figure 5. Contamination-corrected concordant $^{207}Pb/^{206}Pb$ model ages of L chondrites. The L5-L6 chondrites yield a 4551±5 m.y. mean age whereas that of the L3 chondrites is 4537±17 m.y. The Bjurböle data show an anomalously old age of 4588±15 m.y. Open circles denote samples which remained discordant even after removal of all ^{204}Pb as terrestrial.

the concordia curve even when the maximum correction is applied. Thus, it appears that some of the excess radiogenic Pb cannot be attributed to terrestrial Pb contamination alone [18,20]. Given a simple two-stage model (Fig. 4), these discordances imply that Pb was redistributed over areas larger than the samples analyzed during a recent event [18,20].

The age of Bishunpur is much more precise than those of AH77278, so that the mean L3 age (4537±24 m.y.) is essentially that of Bishunpur (4543±16 m.y.). If Bjurböle is included, a best-estimate age of 4560 ± 30 m.y. is obtained for the L3-L4 chondrites. In any case the mean age of the unequilibrated L chondrites is not distinguishable from that of the L5-L6 chondrites.

The 4588±15 m.y. concordant age of Bjurböle poses something of an enigma. If this age dates a real event, then the combined data would support the conclusions of Manhes and Allegrè [5]. That is, the 4588±15 m.y. age of Bjurböle defines the formation of the L chondrite parent body and the ~4550 m.y. age of the L5-L6 chondrites defines the thermal metamorphic event which produced the L5-L6 chondrites.

Alternatively, the old apparent age for Bjurböle could simply reflect over-correction for terrestrial Pb. The

discordancy of this particular aliquot of Bjurböle (Fig. 2) could be real, similar to those of some of the L5-L6 chondrites (Fig. 4; the true location of the Bjurböle data may be on the upward extension of the best-fit line). Since Bjurböle fell through sea ice [23] and is also very friable, the discordancy may also result from U loss due to sea water leaching. The lack of support for this old age from the L3 chondrites, as well as the 4556±13 m.y. $^{207}Pb/^{206}Pb$ model age for Bjurböle when the Pb data are corrected for Cañon Diablo troilite Pb alone (Table 3) tend to support this latter hypothesis.

4.3 Terrestrial-corrected Pb abundances.

The right-hand portion of Table 6 shows the calculated contaminant and indigenous ^{204}Pb concentrations in the whole-rock and troilite separates, again assuming that the U-Pb are concordant and that the Pb in the troilite is a mixture of terrestrial and Cañon Diablo-type Pb. If one considers the possibility of small amounts of recent Pb loss (Fig. 4), then the approximations in Table 6 may slightly underestimate the amount of contaminant ^{204}Pb.

The whole-rocks analyzed apear to contain ~.07-.7 ppb of terrestrial ^{204}Pb. This corresponds to ~5-50 ppb total Pb. In view of the ~200 ppb and 2 ppm of terrestrial Pb

found in Nakhla [40] and Moama [42], respectively, and the large amounts of terrestrial Pb (several ppm) commonly found in meteorite fusion crusts [e.g. 18,22], even the larger amounts of terrestrial Pb do not seem unreasonable. In addition the sintering compounds used in diamond blades are known to contain large amounts of Pb [e.g. 43].

There are no clear cut correlations between the amount of terrestrial Pb and sample handling, although some generalizations can be made. (1) Samples chipped from larger stones which were protected by fusion crusts generally show low amounts of contamination. (2) Both sawn samples (Mezö-Madaras and Harleton) show large amounts of terrestrial contamination. In addition the only "find" analyzed (AH77278) and the most altered sample (Modoc) appear to contain large amounts of terrestrial Pb. The Moama eucrite [42] which was grossly contaminated with terrestrial Pb, was also quite badly oxidized.

The troilite separates generally contain 1-5 times as much terrestrial Pb as the whole-rocks. The reasons why troilite would be enriched in terrestrial Pb relative to the bulk sample are not known. It is, of course, possible that at least some of the contamination was induced during the separation procedures (see also [28]). This could be especially true for the Modoc troilite separate which was

obtained by heavy-liquid separations rather than hand-picking. However, the amount of terrestrial Pb in the troilite separates correlates well with the amount of contaminant Pb in the bulk sample even though sample preparation procedures were quite different (see Sec. 2.1). This suggests that the majority of the contamination occurred prior to separation and analysis.

The calculated amounts of indigenous ^{204}Pb are shown in the last two columns in Table 6. Considering the magnitude of the corrections, the calculated values for the L5-L6 chondrites are reasonably consistent. A mean value of .028±.023 ppb ^{204}Pb is obtained from the mean (unweighted) of the averages of the two analyses for each sample. This corresponds to 1.4±1.1 ppb total initial Pb (assuming this Pb has the isotopic composition of Cañon Diablo troilite Pb). Consequently, calculated contamination-corrected $^{206}Pb/^{204}Pb$ ratios for the L5-L6 chondrites are very radiogenic ($\leq$100-400). Initial Pb concentrations increase drastically from types 5 and 6 to type 3. ^{204}Pb is enriched by a factor of $\sim 4 \times 10^3$ in Mezö-Madaras relative to the L5-L6 chondrites and by a factor of ~60 relative to Bjurböle.

Troilite in these meteorites does not appear to be enriched in indigenous ^{204}Pb relative to the bulk samples. Troilite in the L5-L6 chondrites has approximately the same

amount of Pb as the whole-rock, whereas troilite in the L3-L4 chondrites is depleted in Pb by factors of .11 and .02 in Bjurböle and AH77278, respectively. The lack of enrichment of Pb in troilite has also been observed in another L3 chrondirte, Khohar [44]. In view of possible mineral impurities in the troilite separates (Table 4, and section 3.3), the Pb contents in these separates should probably be viewed as upper limits to the Pb abundances in "pure" troilite.

4.4 Th-U-Pb systematics.

A semi-independent check of the validity of the correction procedures can be obtained from the Th-U-Pb system. As previously mentioned in section 2.2, possible Th contamination in the mass spectrometer filaments prohibits rigorous interpretation of the Th/Pb ages. Indeed, both the Cañon Diablo troilite-corrected data and the chondrite troilite-corrected data are badly scattered on U-Th-Pb concordia diagrams (not shown). The chondrite troilite-corrected data do plot both above and below the concordia curve, whereas the Cañon Diablo-corrected data all plot above it. However, it is not possible in all cases to determine whether the scatter is caused by the correction procedure or is due to small amounts of Th contamination.

Consequently a somewhat less-sensitive approach has been employed.

If it is assumed that the $^{232}Th/^{208}Pb$ should be concordant with the two U-Pb systems (Sec. 4.2), then the $^{232}Th/^{238}U$ ratio required to achieve this concordancy can be calculated. The calculated vs measured $^{232}Th/^{238}U$ ratios are shown in Figure 6. The solid line is the ideal 1:1 correlation. The general agreement between the measured and observed ratios suggests that the correction procedure is approximately valid.

The AH77278 data are anomalous. The location of the data in Figure 6 suggests that either the data are over-corrected for terrestrial Pb, or that both samples were coincidentally run with Th-contaminated filaments. On the other hand, the young concordant ages (Fig. 5) suggest that the data are under-corrected for terrestrial Pb. Sm-Nd analyses of an Antarctic chondrite (N. Nakamura, pers. comm.) and Lu-Hf analyses of an Antarctic eucrite [45] also yielded anomalous results. Presumably, the unique terrestrial history of these meteorites are responsible for the anomalous results. The U-Th-Pb data could perhaps reflect Pb contamination in combination with U and/or Pb loss due to leaching.

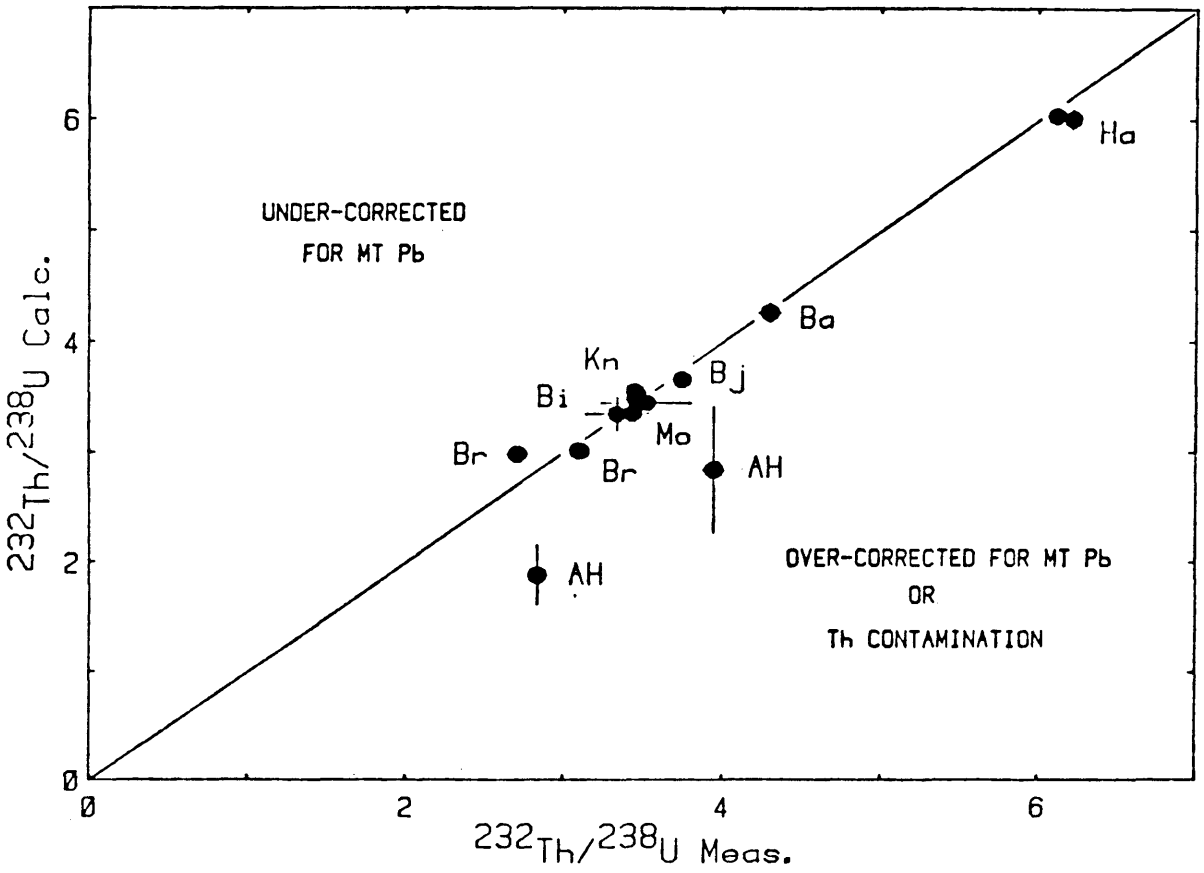

Figure 6. Calculated vs. measured $^{232}Th/^{238}U$ ratios. Ratios are calculated assuming concordancy between the $^{206}Pb/^{238}U$ and $^{208}Pb/^{232}Th$ ages. The solid line is the ideal 1:1 correlation. Data plotting above this line suggest under-correction for modern terrestrial Pb (MT) contamination. Those plotting below the line suggest Th contamination or over-correction for MT Pb.

4.5 L chondrite initial Pb.

A major objective of this study was to determine whether there are any real variations in the initial Pb isotopic compositions of these meteorites. The relatively large amounts of terrestrial Pb contamination in these meteorites prohibit precise calculations of the initial Pb isotopic compositions. However, some observations regarding the apparent initial Pb isotopic composition of the Mezö-Madaras magnetic fraction (Table 5) are worthy of mention.

The blank- and mass fractionation-corrected isotopic compositions and the apparent initial isotopic compositions of the Mezö-Madaras whole-rock and magnetic fraction are shown on an expanded $^{207}Pb/^{204}Pb$ vs $^{206}Pb/^{204}Pb$ plot in Figure 7. Shown for reference are 4550-0 m.y. (heavy solid line), 4580-4550 m.y., and 4550-400 m.y. (light solid lines) isochrons and a mass-fractionation line (broken line; slope ~1.5) through Cañon Diablo troilite Pb (CD). The stippled area represents the field of possible mixtures of "normal" terrestrial Pb and Cañon Diablo Pb.

Also shown by the closed circles are the results of a previous analysis of Mezö-Madaras by Tilton [3]. Both the measured and calculated initial values are identical to those from this work. However, Tilton's preferred interpretation was that the Mezö-Madaras initial Pb was

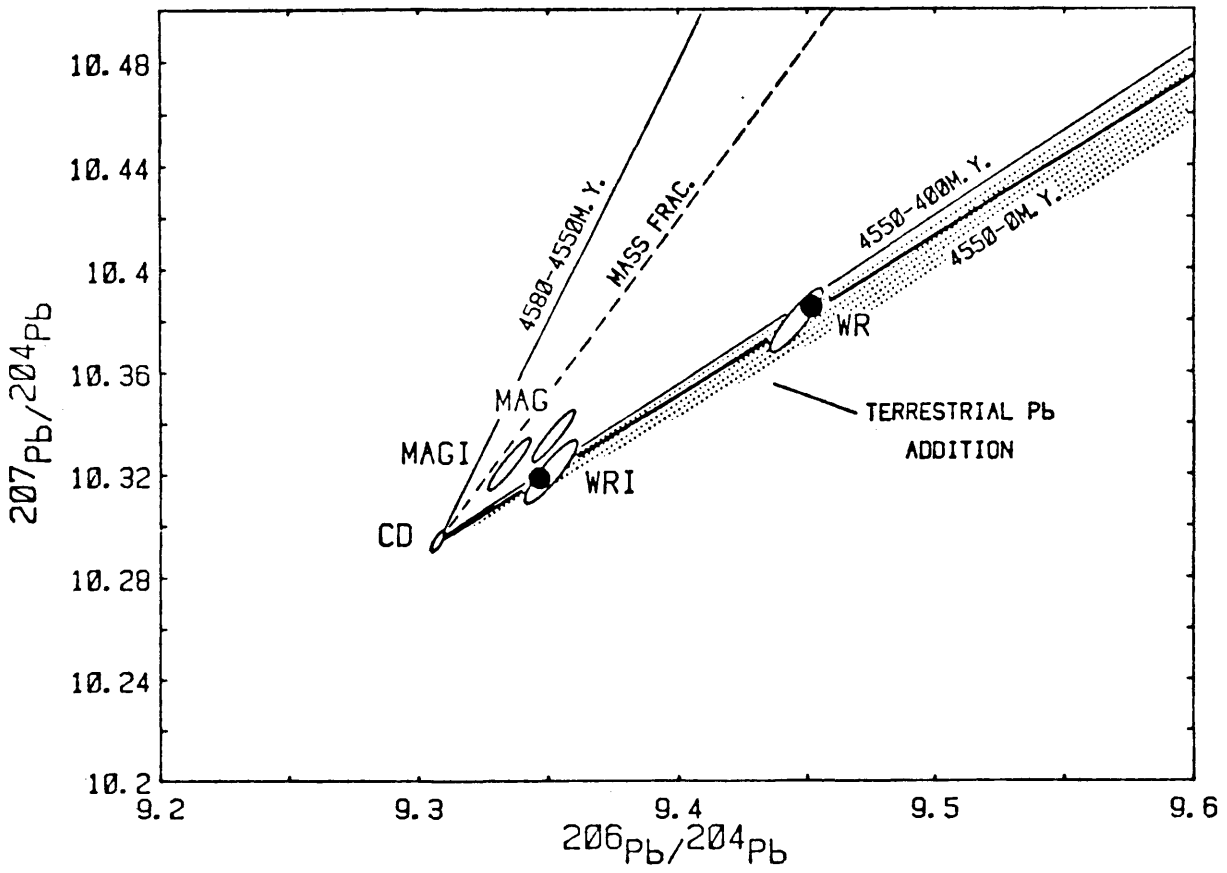

Figure 7. $^{207}Pb/^{204}Pb$ vs. $^{206}Pb/^{204}Pb$ plot of observed and apparent initial Pb's from Mezö-Madaras. WR=whole-rock, MAG=magnetic, I= initial, and CD= Cañon Diablo troilite Pb. The stippled field represents possible mixtures of "normal" terrestrial Pb and CD Pb. The solid circles show Tilton's [3] previous analysis of Mezö-Madaras. Shown for reference are a 4550-0 m.y. (heavy solid line), 4550-400 m.y., and 4580-4550 m.y. (light solid lines) isochrons. The broken line is a mass-fractionation line through CD Pb.

probably the same as that in Cañon Diablo troilite. The whole-rock data plot on the 4550-0 m.y. isochron but the uncertainty overlaps the 4550-400 m.y. isochron. Thus it cannot be determined from this diagram whether the apparent 400 m.y. event (Fig. 3) had any effect on the U-Pb system of this meteorite. The data from the magnetic fraction, on the other hand, plot distinctly above these two reference lines (^{207}Pb-enriched). From Figure 3 it is evident that the whole-rock is not compatible with single-stage evolution from the apparent initial Pb in the magnetic fraction. Furthermore, it is evident from Figure 7 that the deviation of the magnetic separate data from the 4550-0 and 4550-400 m.y. isochrons is not solely due to terrestrial Pb contamination, nor can these data be fully explained in terms of an evolved initial Pb. That is, if closure of the U-Pb system in the L chondrite parent body occurred at ~30 m.y. after that in Cañon Diablo troilite, then the apparent initial Pb isotopic composition would plot with a slope of ~2 relative to Cañon Diablo troilite (e.g. the arbitrary 4580-4550 m.y. reference line). The data can be reconciled by (1) a three-stage U-Pb evolution model, (2) a two-stage model (an evolved initial Pb) + terrestrial Pb contamination, (3) a two-stage model + over-correction of the magnetic separate data for mass fractionation, or (4) a

single-stage model + terrestrial Pb contamination and mass fractionation over-correction.

Recent work on Enstatite chondrites [5,46] has shown that the initial Pb in these meteorites may have been slightly evolved (~0.1-0.2% enriched in ^{207}Pb) relative to Cañon Diablo troilite Pb, yet these meteorites appear to be very old (4577±4 m.y.; [5]). Consequently, one might expect a similar or even greater enrichment of ^{207}Pb in the L chondrites, which appear to be ~30 m.y. younger than the E chondrites. Therefore, solution (2) above would seem to be the most plausible. That is, the U-Pb system of this meteorite, and presumably the other L chondrites, evolved over the last 4550 m.y. from an initial Pb slightly ^{207}Pb enriched relative to Cañon Diablo troilite Pb. Further analyses on other unequilibrated ordinary chondrites will be required to confirm and more precisely define the magnitude of the apparent ^{207}Pb enrichment. For the present, it is perhaps better to emphasize that no evidence has been found for variations in the initial Pb isotopic composition of > 0.3%. The effect of a slightly evolved initial Pb on the other meteorites would be to reduce the concordant model ages of Bishunpur and Bjurböle by as much as ~25m.y. and ~10m.y., respectively. However, the effect on the concordant model ages of the L5-L6 chondrites would be less than 1 m.y.

4.6 4550 m.y.: Formation or metamorphism?

There are currently two general theories regarding volatile element distributions in ordinary chondrites. The good inverse correlation between the volatile element abundances and degree of apparent metamorphism have led several authors [e.g. 47-49] to conclude that the volatile-element-depletions seen in the types 5-6 chondrites are the direct result of (open-system) thermal metamorphism. If the metamorphism model is correct, then the L3 chondrites would define the age of accretion of the meteorite parent body whereas both whole-rock and internal isochrons from L5-6 chondrites would define the age of metamorphism.

Detailed studies of volatile element distributions [e.g. 50,51] have suggested that the volatile element-depleted character of the types 5-6 chondrites is the result of primary accretion. Comparisons between the volatile element abundances in equilibrated ordinary chondrites [52] with those in artificially heated unequilibrated chondrites [e.g. 53] have further suggested that metamorphism did not occur in a system open to volatiles. Given a primary accretion model, the whole-rock isochron age of the L3-4 chondrites would be equal to or perhaps slightly younger than that of the L5-6 chondrites. This age would represent

the accretion age, whereas an internal isochron of a given L5-6 chondrite would define the age of metamorphism.

The concordia intercepts obtained from the internal study of the Barwell chondrite [18], adjusted for the proper U isotopic composition are 4564±4 m.y. and -164±250 m.y., when the data are corrected for the chondrite troilite apparent initial Pb as explained in Section 4.1. The slightly negative lower intercept suggests that the data may be slightly over-corrected for terrestrial Pb contamination. In any case, this 4564±4 m.y. age is not distinguishable from the 4553±8 m.y. age obtained from the L5-6 whole-rock isochron in Figure 4.

Unfortunately, a precise age for the L3-4 chondrites could not be determined (Fig. 5, sections 4.2). If the ~4580 m.y. age of Bjurböle can be confirmed as a real event such as formation of the parent body [5], then the data presented here and in [5] in conjunction with the Barwell data [18], would strongly support the metamorphism model. However, the contamination-corrected age of Bishunpur, as well as the Cañon Diablo troilite-corrected ages of Bjurböle and Mezö-Madaras, suggest that there are no age differences among the various L-chondrites. If this is the true picture, then neither model could be effectively ruled out--the data would merely suggest that accretion and

metamorphism were essentially simultaneous. Consequently the 4553±8 m.y. age (Fig. 4) of the L5-L6 chondrites is interpreted as the equilibration age of the L-chondrite parent body, implying metamorphism. The formation ages, as defined by the mean of the concordant model ages of AH77278, Bishunpur, and Bjurböle is 4560±30 m.y. which is not, at present, distinguishable from the equilibration age. It is hoped that further studies of unequilibrated ordinary chondrites, currently in progress, will permit a more precise determination of the age of these meteorites and thus its significance.

5. CONCLUSIONS

(1) U, Th, and Pb analyses of whole-rock and troilite or magnetic separates from several L chondrites suggest that the excess radiogenic Pb and wide variations in $^{207}Pb/^{206}Pb$ model ages commonly found in ordinary chondrites are the result of terrestrial Pb contamination in these samples prior to analysis. The meteorites analyzed appear to contain from ~5 to 50 ppb terrestrial Pb. The magnitude of the Pb contamination is related to sample handling and degree of alteration.

(2) Pure and uncontaminated troilite in L5-L6 chondrites is essentially U-Th-and Pb-free ($\leq$3ppb Pb).

Furthermore, troilite in L3-L4 chondrites is depleted in Pb by 1-2 orders of magnitude relative to the bulk sample. Consequently, the Pb isotopic composition of the troilite is very sensitive to terrestrial Pb contamination. Therefore, the Pb isotopic composition of the troilite can be used to determine the isotopic composition of the Pb contaminant, and the whole-rock analyses can be accurately corrected for terrestrial Pb contamination.

(3) Two methods for correcting the L5-L6 whole-rock data for terrestrial Pb contamination yield identical ages of 4553±8 m.y. and 4551±5 m.y. The 4553±8 m.y. age is interpreted as the equilibration age (or metamorphism age) of the L5-L6 chondrites. This age is in marginal agreement with the 4564±4 m.y. internal isochron age of Barwell [18] adjusted for the proper U isotopic composition, and in excellent agreement with the 4552 m.y. Pb-Pb model ages of two minimally contaminated L5 chondrites [5]. The contamination-corrected data suggest that some large scale redistribution of Pb (or Pb loss) may have occurred ~400 m.y. ago. Th-U-Pb relationships suggest that the correction procedures are approximately valid.

(4) The L chondrite accretion age as defined by the contamination-corrected, concordant $^{207}Pb/^{206}Pb$ ages of the L3 and L4 chondrites is 4560±30 m.y. This age is, within

error, the same as that of the L5-6 chondrites, but the large uncertainty in this age does not exclude the possibility that accretion preceded metamorphism by as much as 30 m.y. [5].

(5) Determination of a precise age for the unequilibrated L chondrites is further complicated by the possibility that the initial Pb isotopic composition of the L chondrites was slightly ^{207}Pb-enriched (evolved) relative to Cañon Diablo troilite Pb. Evidence for this evolved initial Pb is strongly suggested by the Pb data from the Mezö-Madaras magnetic separate, and to a much lesser extent by the Bishunpur magnetic-separate data.

6 REFERENCES

1. N. H. Gale, J. W. Arden and R. Hutchinson, Uranium-lead chronology of chondritic meteorites, Nature 240 (1972) 56-57.

2. M. Tatsumoto, R. J. Knight and C. J. Allegrè, Time difference in the formation of meteorites as determined from the ratio of lead-207 to lead-206, Science 180 (1973) 1279-1283.

3. G. R. Tilton, Isotopic lead ages of chondritic meteorites, Earth Planet. Sci. Lett. 19 (1973) 321-329.

4. J. M. Huey and T. P. Kohman, ^{207}Pb-^{206}Pb isochron and age of chondrites, J. Geophys. Res. 78 (1973) 3227-3244.

5. G. Manhes and C. J. Allegrè, Time differences as determined from the ratio of lead-207 to lead-206 in concordant meteorites, Meteoritics 13 (1978) 543-548.

6. G. W. Reed, K. Kigoshi, and A. L. Trukevich, Determinations of Heavy elements in meteorites by activation analysis, Geochim. Cosmochim. Acta 20, (1960), 122-140.

7. G. Turner, Thermal Histories of meteorites by the ^{39}Ar-^{40}Ar method, In: Meteorite Research (P. M. Millman, Ed.)., Dordrecht, Reidel (1969) 407-417.

8. D. D. Bogard, L. Husain and R. J. Wright, ^{40}Ar-^{39}Ar

dating of collisional events in chondrite parent bodies, J. Geophys. Res. 81 (1976) 5664-6578.

9. G. Turner, J. A. Miller and R. L. Grasty, The thermal history of the Bruderheim meteorite, Earth Planet. Sci. Lett. 1 (1966) 155-157.

10. K. Gopalan and G. W. Wetherill, Rubidium-strontium studies on black hypersthene chondrites: Effects of shock and reheating, J. Geophys. Res. 76 (1971) 8484-8492.

11. J. F. Minster and C. J. Allegrè, ^{87}Rb-^{87}Sr dating of L chondrites: Effects of Shock and Brecciation, Meteorites 14 (1979) 235-248.

12. D. M. Unruh, N. Nakamura and M. Tatsumoto, History of the Pasamonte achondrite: relative susceptibility of the Sm-Nd, Rb-Sr and U-Pb systems to metamorphic events, Earth Planet. Sci. Lett. 37 (1977) 1-12.

13. J. H. Chen and G. R. Tilton, Isotopic lead investigations on the Allende carbonaceous chondrite, Geochim. Cosmochim. Acta 40 (1976) 635-643.

14. M. Tatsumoto, D. M. Unruh, and G. A. Desborough, U-Th-Pb and Rb-Sr systematics of Allende and U-Th-Pb systematics of Orgueil, Geochim. Cosmochim. Acta 40 (1976) 617.634.

15. N. H. Gale, J. W. Arden and R. Hutchison, U-Pb studies

of the Appley Bridge meteorite, Naturwissenschaften 66 (1979) 419-420.

16. A. G. W. Cameron, Are large time differences in meteorite formation real? Nature 246 (1973) 30-32.

17. J. T. Wasson, Meteorites (Chap. XVIII), Springer-Verlag, New York (1974) 181-205.

18. D. M. Unruh, R. Hutchison and M. Tatsumoto, U-Th-Pb age of the Barwell chondrite: anatomy of a discordant meteorite, Proc. Lunar. Planet. Sci. Conf. 10th (1979) 1011-1030.

19. M. C. B. Abranches, J. W. Arden and N. H. Gale, Uranium lead abundances and isotopic studies in the chondrites Richardton and Farmington, Earth Planet. Sci. Lett. 46 (1980) 311-322.

20. N. H. Gale, J. W. Arden, and M. C. B. Abrances, Uranium-lead age of the Bruderheim L6 chondrite and the 500-Ma shock event in the L-group parent body, Earth Planet. Sci. Lett. 48 (1980) 311-324.

21. V. M. Oversby, Lead, In: Handbook of Elemental Abundances in Meteorites, Gordon and Breach, New York, (1971) 499-510.

22. D. M. Unruh, M. Tatsumoto, and R. Hutchison, U-Pb study of the Richardton H5 chondrite, Meteoritics 14, 551-553.

23. M. H. Hey, Catalogue of Meteorites (Alden Press, G. B.) 637 pp. 24. R. Hutchison, A. W. R. Bevan, and J. M. Hall, Appendix to the Catalogue of Meteorites (Benham Press, G. B.) 297 pp.

25. R. T. Dodd and E. Jarosewich, Incipient melting and shock classification of L-group chondrites, Earth Planet Sci. Lett. 44 (1979) 335-340.

26. R. T. Dodd and E. Jarosewich, Covariation of iron and sulfur in low-iron ordinary chondrites, Meteoritics 14 (1979) 380-381.

27. B. Mason In: Anarctic Meteorite Newsletter 1, NASA, (1978) 35.

28. G. R. Tilton and J. H. Chen, Lead isotope systematics of three Apollo 17 mare basalts, Proc. Lunar. Planet. Sci. Conf. 10th (1979) 259-274.

29. M. Tatsumoto and D. M. Unruh, KREEP basalt age: Grain by grain U-Th-Pb systematics study of the quartz-monzodiorite clast 15405.88, Proc. Lunar. Sci. Conf. 7th (1976) 2107-2129.

30. K. R. Ludwig, Calculation of uncertainities of U-Pb isotope data, Earth Planet. Sci. Lett. 46 (1980) 212-220.

31. G. Crozaz, Uranium and thorium micro distributions in stony meteorites, Geochim. Cosmochim. Acta 43 (1979)

127-136.

32. J. C. Laul, I. Z. Pelley, and M. F. Lipschutz, Thallium contents of chondrites, Geochim. Cosmochim. Acta 34 (1970) 909-920.

33. J. C. Laul, D. R. Case, F. Schmidt-Bleek, and M. F. Lipschutz, Bismuth contents of chondrites, Geochim. Cosmochim. Acta 34 (1970) 89-103.

34. D. R. Case, J. C. Laul, I. Z. Pelley, M. A. Wechter, F. Schmidt-Bleek, and M. F. Lipschutz, Abundance patterns of thirteen trace elements in primitive carbonaceous and unequilibrated ordinary chondrites, Geochim. Cosmochim. Acta 37 (1973) 19-33.

35. D. Heyman, The noble gases In: Handbook of Elemental Abundances in Meteorites, Gordon and Breach, New York (1971) 29-66.

36. G. W. Reed and S. Jovanovic, Mercury in chondrites, J. Geophys. Res. 72 (1967) 2219-2228.

37. J. H. Chen and G. J. Wasserburg, A search for isotopic anomalies in uranium, Geophys. Res. Lett. 7 (1979) 275-278.

38. D. York, Least squares fitting of a straight line with correlated errors, Earth Planet. Sci. Lett. 5 (1969) 320-324.

39. G. W. Wetherill, Discordant Uranium-lead ages, Trans.

Amer. Geophys. Union 37 (1956) 320-326.

40. N. Nakamura, D. M. Unruh, and M. Tatsumoto, The young magmatic event in the Nakhla achondrite parent body, In: Short Papers of the Fourth International conference, Geochronology, Cosmochronology, Isotope Geology (R. E. Zartman ed.), U.S.G.S. Open-File Report 78-701 (1978) 305-306.

41. F. Oberli, J. C. Huneke, and G. J. Wasserburg, U-Pb and K-Ar systematics of cataclysm and precataclysm lunar impactites, In: Lunar and Planetary Science X, The Lunar Science Institute, Houston (1979) 940-942.

42. J. Hamet, N. Nakamura, D. M. Unruh, and M. Tatsumoto, Origin and History of the adcumulate eucrite, Moama, as inferred from REE abundances, Sm-Nd and U-Pb systematics, Proc. Lunar Planet Sci. Conf. 9th (1978) 1115-1136.

43. P. D. Nunes, D. M. Unruh, and M. Tatsumoto, U-Th-Pb systematics of Apollo 16 samples 60018, 60025, and 64435; and the continuing problem of terrestrial Pb contamination of Lunar samples, Lunar Research 1 (1977) 61-69.

44. D. S. Woolum, R. Mascitelli, D. S. Burnett, and L. S. August, Evidence for the siderophilic behavior of meteroritic bismuth, Proc. Lunar. Planet. Sci. Conf.

9th (1978) 1173-1186.

45. P. J. Patchett and M. Tatsumoto, Lu-Hf total-rock isochron for the Eucrite meteorites, Nature (in Press).

46. D. M. Unruh and M. Tatsumoto, U-Pb study of Abee consortium samples, Meteoritics (in Press).

47. J. A. Wood, Chondrites: Their metallic minerals thermal histories and parent planets, Icarus 6 (1967) 1-49.

48. R. T. Dodd, Metamorphism of ordinary chondrites, Geochim. Cosmochim. Acta 33 (1969) 161-203.

49. J. T. Wasson, Formation of ordinary chondrites, Rev. Geophys, Space Phys. 10 (1972) 711-759.

50. J. W. Larimer and E. Anders, chemical fractionations in Meteorites II Abundance patterns and their interpretation, Geochim. Cosmochim. Acta 31 (1967) 1239-1270.

51. P. R. Keays, R. Granapathy, and E. Anders, chemical fractionations in meteorites-IV. Abundances of 14 trace elements in L chondrites; implications for cosmothermonometry. Geochim. Cosmochim. Acta 35 (1971) 337-363.

52. H. Takahashi, J. Gros, H. Higuchi, J. W. Morgan, and E. Anders, Volatile elements in chondrites: metamorphism or nebular fractionation, Geochim. Cosmochim. Acta 42