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Chemical studies of L chondrites. VI: Variations with petrographic type and shock-loading among equilibrated falls

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Abstract—To study compositional trends associated with open and closed system metamorphism and/or shock-induced heating of the L4-6 chondrite parent(s), we used ICPMS and RNAA to quantify 51 trace elements in 48 chemically representative fall samples. With these data, we used graphic and two multivariate statistical methods for examining evidence for compositional differences with respect to petrographic type and degree of shock loading. Comparisons of mildly shocked (S1-S3) L5 and L6 suites (9 and 8 chondrites, respectively) yield no convincing statistical evidence for a difference in trace element content. Our multivariate comparisons show a difference on a model-dependent basis, but yield indeterminate results on a model-independent basis. Compositionally, suites of strongly shocked (S4-S6) and mildly shocked L4-6 chondrites (26 and 19 samples, respectively) can be distinguished at statistically significant levels on both model-dependent and -independent bases. In the strongly shocked suite, contents of refractory lithophiles are higher, and siderophiles and volatiles are lower than those of the mildly shocked suite at moderately ($p \leq 0.05$) to highly significant ($p \leq 0.01$) levels. Our studies suggest that chemical differences from vaporization and loss of volatiles along with metal/silicate partitioning are present from extended cooling of shock-heated bodies produced by intermittent impacts, especially the massive impact(s) that disrupted the L chondrite parent(s) ~500 Ma ago. *Copyright © 2004 Elsevier Ltd*

1. INTRODUCTION

In principle, the chemical composition and mineralogic and textural properties of chondrites record the genetic processes that converted nebular gas and dust into primitive parent materials which could then be metamorphosed (e.g., McSween et al., 1988) and ejected as collisional debris from their parent bodies. Each of these primary, secondary and tertiary episodes, respectively, could be accompanied by substantial heating leading to compositional alterations if the system were open to material transfer.

Before this study, only that of Kallemeyn et al. (1989) reported data for over a dozen elements in a large number (66) of ordinary chondrites. That study of ~20 each of H3-6, L3-6 and LL3-6 chondrites (some of which were finds) focused on primary elemental fractionations. Since their element suite included but 2 highly mobile elements, the data of Kallemeyn et al. (1989) are not especially instructive for postaccretionary thermal fractionations.

Trace elements provide the best compositional markers of such episodes since small absolute amounts of element transferred should be multiplied into large relative compositional changes. The generation of a database for 49 trace elements in 45 L4-6 chondrite falls, also characterized as to shock history, is no modest task. These data, which include highly labile elements, are especially valuable since they were, on the whole, generated by the same analysts using the same techniques, ICPMS and RNAA, for homogenized, representative samples, thereby essentially eliminating obfuscating problems of sample heterogeneity and terrestrial contamination.

In the past, we focused on the most thermally labile trace elements—particularly Rb, Cs, Se, Ag, Te, Zn, In, Bi, Tl and Cd—since these are most sensitive to genetic processes accompanied by significant heating (Lipschutz and Woolum, 1988; cf. Matza and Lipschutz, 1977; Tonui et al., 2003, and references therein). These include the most volatile elements, i.e., those forming solids at the lowest temperatures during (primary) nebular condensation and accretion, and the most mobile ones, i.e., the elements most easily vaporized and lost during (secondary) thermal metamorphism and (tertiary) cooling of shock-heated parent material. While volatile elements are thermally mobile ones and vice versa, their lability orders differ. In this study we choose to order them (as above) by increasing lability at 1000°C, both because this has been experimentally determined (e.g., Ikramuddin et al., 1977) and because compositional trends in L4-6 chondrites confirm this tertiary process as a dominant one (Walsh and Lipschutz, 1982; Huston and Lipschutz, 1984).

In an earlier study focusing upon labile trace elements, Lingner et al. (1987) found that the two most numerous chondritic groups, H4-6 and L4-6, compositionally differ markedly because of differences in dominant genetic processes. Those L4-6 chondrites that escaped being strongly shock-loaded during their history (i.e., S1-S3) and, thus, were heated to but a small degree, contain much higher levels of mobile trace elements than do similar, mildly shocked H4-6 chondrites. Additionally, as a group, the L4-6 chondrite history is dominated by at least one episode of intense shock-loading (that the H4-6 largely escaped), culminating in the disruption of their parent(s). In many cases, postshock temperatures reached

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≥1500°C, (Stöffler et al., 1988) with lesser levels of residual heat persisting for months to years, i.e., long enough for the collisional debris to lose their full complement of radiogenic ^{40}Ar and/or ^{4}He (and other elements as found e.g., by Huston and Lipschutz, 1984) and date the major impact event at ~500 Ma ago (Anders, 1964; cf. Bogard et al., 1976; Bogard and Hirsch, 1980; Schmitz et al., 2003). These factors make the L chondrites an ideal subject for studying the effects of shock on chemical composition.

The evidence that strongly shocked L4-6 chondrites were heated much more than were mildly shocked ones is so compelling that loss of labile trace elements with radiogenic gases is unquestioned. Multivariate statistical analysis (Lipschutz and Samuels, 1991) of L4-6 chondrite falls based on 11 mobile trace elements reveals perfect separation of mildly and strongly shocked subsets using model-dependent linear discriminant analysis (LDA) and logistic regression (LR). However, as Lipschutz and Samuels (1991) noted, model-dependent significance levels are artifacts of the quantity of available data for labile trace elements. Given sufficient data, even the smallest mean concentration differences can prove highly significant. For example, Lipschutz and Samuels (1991) demonstrated that, using randomization-simulations involving these subsets, separations are over determined. Thus, on a model-independent basis, the compositional differences could not be confirmed statistically (Lipschutz and Samuels, 1991). Using the metric of LR and data for the 4 least mobile trace elements, the model-independent significance level reached 0.009: analysis using the LDA metric always yielded inconclusive results no matter how many (or few) of the 11 mobile trace elements were considered. Lipschutz and Samuels (1991) noted in this connection their expectation that additional compositional data for less labile elements and an expanded sample suite, particularly with additional mildly shocked L4-6 falls, could prove statistically significant.

There is no reason to believe that only highly mobile trace elements should be markers for shock-loading. More refractory elements should record high-temperature episodes, by loss or even enrichment, as mobile species are lost. Of course, the compositional changes involving these elements should be subtler than those of more labile elements. Earlier, we demonstrated that ICPMS is capable of producing accurate and precise data for a large number of more refractory lithophile and siderophile trace elements (Friedrich et al., 2002). Consequently, we decided to apply this technique (accompanied by RNAA) to L4-6 chondrite falls to consider three questions:

1. Do the ICPMS/RNAA data provide unambiguous compositional evidence for secondary (parent body) metamorphism?

2. Do contents of trace elements other than highly mobile ones record late shock-heating?

3. Do multivariate statistical techniques yield more conclusive, model-independent evidence for thermally induced chemical fractionation when data for more elements in additional L4-6 falls are available?

2. EXPERIMENTAL

2.1. Meteorite Samples

In Table 1 we list the 48 L4-6 chondrite falls included in this study, with sample sources and other details. Our initial suite included 62 L falls: however, 14 exhibited fractionated REE patterns suggestive of sample heterogeneity, mainly resulting from small sample sizes (Friedrich et al., 2003) and we omit them from consideration here. Of the 48 samples analyzed by ICPMS and RNAA for this study, 41 were aliquots of the same homogenized sample powder. In five other cases, we analyzed different portions of a sample from the same institution (Table 1). Three of these (Bruderheim, Louisville light; Wethersfield (1971), analyzed as chips by RNAA, were portions of the same whole-rock specimen ground for the Smithsonian Meteorite Powder Collection (SMPC) and analyzed by ICPMS. Two others (Farmington, Tennasilm) were whole-rock fragments from the same specimen. Only for Ramsdorf and Saratov did we use material from different specimens for ICPMS and RNAA (Table 1). Friedrich et al. (2003) addressed the issue of representative sampling and concluded that careful selection of ≥ 10 g of visually representative material (metal and silicate) results in acceptable analytical accuracy and precision (Wilson, 1964; Jarosewich, 1990): over 90% of samples in this study derive from such material.

Shock classifications reported in Table 1 are from this study except where otherwise noted. Two similar, and nearly equivalent, shock classification schemes exist: the shock classification system of Stöffler et al. (1991) and coworkers is widely accepted today. The shock-induced mineralogic/petrographic changes of the Stöffler et al. (1991) scale correspond to residual (postshock) temperature rises of: S1, 10–20°C; S2, 20–50°C; S3, 100–150°C; S4, 250–350°C; S5, 600–850°C; S6, 1500–1750°C. Smith and Goldstein (1977) estimated annealing times for strongly shocked L5,6 chondrites from metallographic cooling rates as days to 10^4 years, i.e., more than ample for volatiles to be lost (cf. Bogard et al., 1976; Walsh and Lipschutz, 1982; Huston and Lipschutz, 1984). In eight cases (Karkh, Kuttippuram, Louisville light, Shelburne, Tuan Tuc, Valdinizza; Wethersfield, 1971, 1982), we converted the shock facies classification, a–f, of Dodd and Jarosewich (1979) to shock stage values, S1-S6 (Stöffler et al., 1991). Of these, Wethersfield (1971) and Wethersfield (1982) were first classified by Clarke et al. (1987), while Louisville light's shock classification is from Huston and Lipschutz (1984); the others were classified by Dodd and Jarosewich (1979). Of the remaining 33 chondrites, shock stage values were not previously known for Saratov, Tennasilm, Ausson, Leedy and Elenovka. Prior shock stage and/or shock facies previously assigned to the remaining 28 chondrites agreed with our assignment listed in Table 1 to ±1 U, the uncertainty normally assumed. We found no petrographic type disagreements with prior ones.

2.2. Analytical Methods

We determined 51 elements by RNAA and ICPMS in each of the 48 L4-6 falls, 9 by both methods. We quantified 15 elements by RNAA (listed by increasing Z): Co, Zn, Ga, As, Se, Rb, Ag, Cd, In, Sb, Te, Cs, Au, Tl, Bi) and 45 elements by ICPMS (Li, Sc, Ti, V, Mn, Co, Cu, Zn, Ga, As, Se, Rb, Sr, Y, Zr, Nb, Mo, Ru, Pd, Sn, Sb, Te, Cs, Ba, REE, Hf, W, Re, Ir, Pt, Th, U).

For the 25 samples measured by RNAA in this study, sample and monitor preparation, irradiation conditions, chemical processing, counting, and data reduction procedures were those used routinely in our laboratory (e.g., Wolf and Lipschutz, 1995a). Because of its small mass (Table 1), Utrecht was irradiated for 4 d at the University of Missouri Research Reactor at a flux of 8×10^{13}/cm^2 s; the other 24 were irradiated for 2 d at the same flux. Chemical yields were ≥30% for each element in the samples and >50% for each element in monitors.

We described our ICPMS technique in previous studies (Friedrich et al., 2002, 2003): additional details are in Friedrich (2002). Here it is sufficient to note that we analyzed meteorite solutions using internal standards (Be, In, Re, Tl) for drift control and used external calibration (with the Allende Standard Reference Meteorite) for additional drift control and external calibration. Allende calibration values are available in Friedrich et al. (2003).

2.3. Statistical Methods

To assist in data interpretation, we use the multivariate statistical methods of LDA and LR, which provide important classification, hence genetic, information for chondrites (Lipschutz and Samuels, 1991;

Table 1. L chondrite falls, type, shock classification, sample sources and nature of samples analyzed by ICPMS and RNAA.

Meteorite	Abbr.	Petr. type	Shock[a]	Remarks	Sample source[b]	Chemical analysis	
						ICPMS[c]	RNAA[d]
Atarra	ATA	4	S3		SMPC		188
Bald Mountain	BLM	4	S4		SMPC		b (SMPC)
Rio Negro	—	4	S2	Regolith breccia	SMPC		197
Saratov	SAR	4	S3		SMPC		b (SMPC), d (ASU 740)
Tennasilm	TEN	4	S3		USNM 483	*0.3474*	a (USNM 483)
Ausson	AUS	5	S3		SMPC		b (SMPC)
Baszkówka	BAZ	5	S1[a]		PGI	9.938	213
Crumlin	CRU	5	S4		SMPC		b (SMPC)
Elenovka	ELV	5	S3		SMPC		b (SMPC)
Farmington	FAR	5	S4		FMNH Me 374	*0.7736*	c (Me 374)
Guibga	GUI	5	S3		SMPC		190
Homestead	HOM	5	S4		SMPC		203
Honolulu	HLU	5	S3		SMPC		187
Innisfree	INN	5	S2[b]		GSC #0906-09	9.768	216
Jhung	JHU	5	S3		SMPC		b (SMPC)
Malakal	MAL	5	S4		SMPC		c (SMPC)
Monte das Fortes	MDF	5	S3	Some brecciation	USNM 6298	1.050	224
Shelburne	SHL	5	S4	Shock facies d	SMPC		203
Tané	TAN	5	S3	Brecciated	USNM 1428	0.5737	201
Apt	APT	6	S4		SMPC		b (SMPC)
Aumale	AUM	6	S4		SMPC		b (SMPC)
Bruderheim	BRU	6	S4		SMPC		c (USNM 2272)
Chantonnay	CHA	6	S4		SMPC		b (SMPC)
Denver	DEN	6	S4[b]		SMPC		197
Girgenti	GIR	6	S4		SMPC		186
Karkh	KAK	6	S4–S5	Shock facies e	SMPC		180
Kunashak	KUN	6	S4		SMPC		175
Kuttippuram	KUT	6	S3	Shock facies c	SMPC		c (SMPC)
Kyushu	KYU	6	S5		SMPC		213
La Criolla	LAC	6	S4[b]		SMPC		185
L'Aigle	LAL	6	S3		SMPC		b (SMPC)
Leedey	LED	6	S4	Polymict breccia	SMPC		221
Louisville dark	—	6	—	Clast(s) in light matrix	SMPC		-
Louisville light	LOU	6	S4	Shock facies d	SMPC		d (USNM 5872)
Modoc (1905)	MOD	6	S4		SMPC		220
Nejo	NEJ	6	S3		SMPC		207
New Concord	NEW	6	S4		SMPC		250
Paranaiba	PAR	6	S6[c]		SMPC		228
Ramsdorf	RAM	6	S4		USNM 1801	*0.6159*	c (ASU 703.1)
Segowlie	SEG	6	S3	Marginal S2 shock	SMPC		215
Tathlith	TAT	6	S3[b]		SMPC		c (SMPC)
Tourinnes-la-Grosse	TLG	6	S3		SMPC		b (SMPC)
Tuan Tuc	TTU	6	S4–S5	Shock facies e	SMPC		b (SMPC)
Utrecht	UTR	6	S3		USNM 1171	0.7603	114
Valdinizza	VAL	6	S4	Shock facies d	SMPC		216
Vouillé	VOU	6	S4		SMPC		b (SMPC)
Wethersfield (1971)	W71	6	S4	Shock facies d	SMPC		d (USNM 5596)
Wethersfield (1982)	W82	6	S3	Shock facies b	SMPC		189

[a] Shock classifications this work except: a. Stepniewski *et al.* (1998); b. Rubin (1994); c. Stöffler *et al.* (1991). Shock facies equivalent (Dodd and Jarosewich, 1979) used when noted in remarks (see text).

[b] SMPC (Smithsonian Meteorite Powder Collection): Smithsonian Institution, Washington D.C.; FMNH: Field Museum Natural History, Chicago; GSC: Geological Survey Canada, Ottawa; PGI: Państwowy Geologiczny Instytut, Warsaw; USNM: Smithsonian Institution, Washington D.C.

[c] Where 4-digit sample masses (g) are listed in normal type, they signify the mass of sample homogenized at Purdue to provide material for both ICPMS and RNAA. Masses in *italics* indicate amount taken to prepare homogenized sample for ICPMS only. All other samples were homogenized material from the SMPC. For ICPMS, we analyzed 3 replicates of 100 mg except two 100 mg replicates of Elenovka and Tathlith (see text, Table 2).

[d] If three-digit number listed, this is sample mass (in mg) of the same homogenized powder analyzed by RNAA in this study. If letter (and source) listed, chondrite was analyzed previously by: a. Binz *et al.* (1976); b. Neal *et al.* (1981); c. Walsh and Lipschutz (1982); d. Huston and Lipschutz (1984). Where (SMPC) is listed in last column, RNAA sample was aliquant of same powder used for ICPMS.

Wolf and Lipschutz, 1995b, 1998; Wolf et al., 1997 and references in them). These methods are more useful than univariate techniques for compositional comparisons because they utilize information from many elements simultaneously. In fact, their pattern recognition ability is widely used for detecting counterfeit money (using six easily measurable parameters such as length and width of bank notes, etc.) and identifying criminal suspects in crowds in real time (Flury and Riedwyl, 1988; Chen et al., 2000; cf. Jain et al., 2000).

In statistical studies, we define two sample subsets (or suites) defined by petrographic type and/or degree of shock-loading and compare them compositionally to assess the extent to which compositional classification parallels petrographic classification. Like previous studies (Lip-

Table 2a. Trace element results for L chondrites (Z = 3–38).[a]

Meteorite	Class	Li (μg/g)	Sc (μg/g)	Ti (μg/g)	V (μg/g)	Mn (mg/g)	Co (μg/g)		Cu (μg/g)	Zn (μg/g)		Ga (μg/g)		As (μg/g)		Se (μg/g)		Rb (μg/g)		Sr (μg/g)
Atarra	L4	1.9	8.39	717	73	2.65	567	*528*	118	72.6	*63.0*	6.26	*6.41*	1.53	-	8.80	*10.1*	2.98	*2.59*	8.8
Bald Mountain[3]	L4	1.5	8.14	671	72	2.58	594	*610*	138	57.6	-	5.38	*4.53*	1.66	*1.4*	13.5	-	2.58	*2.32*	8.5
Rio Negro	L4	2.2	8.18	701	72	2.59	645	*494*	96	362	*291*	5.73	*5.61*	1.77	-	9.38	*8.59*	3.34	*2.82*	8.7
Saratov[2]	L4	1.6	8.90	730	73	2.68	553	*548*	114	68.4	*63.5*	6.03	*5.36*	1.47	*1.2*	8.61	*8.84*	3.43	*2.74*	9.3
Tennasilm[1]	L4	1.6	8.85	694	71	2.52	582	*720*	98	53.7	*59.0*	5.24	*5.7*	1.50	*0.32*	8.17	*6.5*	2.32	-	9.0
Ausson[3]	L5	1.6	8.20	663	67	2.59	628	*636*	101	61.5	*54.3*	5.54	*5.56*	1.77	*1.9*	9.04	-	2.74	*2.25*	8.8
Baszkówka	L5	1.6	8.45	642	66	2.60	549	*270*	109	68.5	*55.6*	6.13	*5.93*	1.66	-	9.76	*8.83*	1.86	*1.38*	8.6
Crumlin[3]	L5	1.6	8.13	673	71	2.62	619	*504*	105	78.8	*47.6*	5.53	*5.07*	1.66	*1.0*	9.37	-	2.83	*2.19*	8.8
Elenovka[3]	L5	1.8	8.53	678	66	2.71	456	*608*	107	60.3	*70.3*	5.49	*5.59*	1.46	*1.35*	10.7	-	2.60	*1.61*	8.6
Farmington[4]	L5	1.6	8.29	579	65	2.68	677	*544*	95	40.0	*52.8*	6.05	*6.20*	1.51	-	7.52	*6.97*	1.59	*1.6*	8.5
Guibga	L5	1.6	8.08	642	66	2.56	758	*213*	94	67.6	*49.3*	5.51	*5.48*	1.98	-	8.94	*9.84*	2.63	*2.02*	8.5
Homestead	L5	1.6	8.14	629	65	2.57	567	*503*	105	54.0	*56.6*	5.43	*6.49*	1.69	-	9.93	*9.95*	2.72	*2.31*	8.6
Honolulu	L5	1.6	8.11	601	63	2.57	570	*417*	109	56.0	*52.0*	5.49	*6.21*	1.51	-	10.5	*10.1*	2.91	*2.74*	8.4
Innisfree	L5	1.6	8.10	597	64	2.61	581	*589*	111	51.3	*38.9*	5.46	*5.12*	1.41	-	9.53	*9.43*	2.64	*2.23*	8.5
Jhung[3]	L5	1.6	8.51	674	66	2.70	523	*571*	113	59.2	*64.2*	5.17	*5.02*	1.50	*1.35*	10.4	-	1.88	*1.01*	8.9
Malakal[4]	L5	1.7	8.50	697	75	2.71	566	*560*	100	57.6	*45.9*	5.60	*5.10*	1.64	-	9.66	*5.83*	2.33	*2.1*	9.2
Monte das Fortes	L5	1.6	7.60	613	76	2.68	490	*561*	107	46.4	*56.7*	5.66	*4.22*	1.57	-	8.60	*8.24*	1.77	*1.30*	9.1
Shelburne	L5	1.6	8.29	655	73	2.60	523	*273*	88	60.6	*41.9*	5.28	*4.79*	1.53	-	7.28	*6.17*	2.26	*1.81*	8.5
Tané	L5	1.6	8.08	592	63	2.70	583	*535*	83	54.2	*47.4*	4.91	*6.07*	1.62	-	9.27	*8.03*	2.09	*1.75*	8.2
Apt[3]	L6	1.7	8.23	663	70	2.64	520	*561*	115	76.4	*56.4*	5.89	*5.31*	1.50	*1.35*	9.93	-	2.84	*2.18*	9.2
Aumale[3]	L6	1.8	8.42	685	72	2.66	559	*520*	98	60.5	*41.3*	5.68	*5.12*	1.52	*1.0*	10.6	-	2.63	*1.77*	9.3
Bruderheim[4]	L6	1.5	7.84	602	57	2.52	538	*351*	120	54.4	*61.6*	5.39	*4.10*	1.63	-	10.4	*7.73*	2.53	*2.4*	8.5
Chantonnay[3]	L6	1.8	8.28	684	76	2.65	556	*526*	100	65.6	*42.4*	5.68	*5.36*	1.54	*1.4*	9.15	-	2.62	*1.73*	8.9
Denver	L6	1.7	8.67	701	72	2.67	554	*373*	85	63.1	*51.8*	5.71	*4.95*	1.49	-	9.66	*8.79*	3.11	*2.03*	9.3
Girgenti	L6	1.6	8.28	621	62	2.61	620	*372*	102	54.5	*42.5*	5.33	*5.20*	1.64	-	9.82	*9.92*	2.70	*1.94*	8.6
Karkh	L6	1.8	8.01	643	73	2.64	578	*471*	114	58.0	*44.0*	5.04	*5.16*	1.55	-	11.1	*11.5*	2.20	*2.82*	8.6
Kunashak	L6	1.9	8.23	621	66	2.63	545	*438*	99	41.1	*35.4*	5.48	*5.67*	1.62	-	10.2	*9.97*	1.70	*1.69*	10
Kuttippuram[4]	L6	1.5	7.88	738	63	2.43	778	*966*	122	69.0	*159*	5.56	*5.80*	1.58	-	11.1	*8.46*	2.04	*3.4*	9.2
Kyushu	L6	1.6	8.56	647	70	2.60	560	*446*	99	57.8	*54.0*	5.43	*5.79*	1.57	-	9.48	*9.85*	2.19	*1.91*	9.1
La Criolla	L6	1.7	8.37	629	72	2.67	505	*261*	96	66.7	*41.6*	5.48	*4.94*	1.61	-	11.1	*8.63*	2.98	*2.02*	8.9
L'Aigle[3]	L6	1.6	8.30	647	71	2.61	608	*602*	99	53.8	*41.6*	5.44	*5.14*	1.64	*0.8*	10.7	-	2.37	*2.28*	8.7
Leedey	L6	1.8	8.34	744	71	2.64	578	*506*	138	58.1	*53.0*	5.87	*5.63*	1.54	-	9.45	*9.05*	2.65	*2.73*	8.8
Louisville dark	L6	2.0	8.26	715	74	2.69	627	-	113	44.6	-	5.21	-	1.55	-	10.5	-	2.05	-	8.5
Louisville light[2]	L6	1.8	8.53	648	77	2.65	540	*287*	92	54.4	*27.3*	5.38	*4.51*	1.51	-	9.41	*5.41*	2.16	*1.9*	8.7
Modoc (1905)	L6	1.6	8.30	615	64	2.63	519	*409*	101	60.3	*58.9*	5.44	*5.37*	1.46	-	9.84	*12.7*	3.00	*2.83*	9.1
Nejo	L6	1.7	8.20	634	66	2.67	589	*472*	106	70.7	*44.7*	5.60	*5.61*	1.57	-	10.7	*10.5*	2.70	*1.97*	8.9
New Concord	L6	1.7	8.26	652	71	2.64	572	*312*	107	61.7	*41.2*	5.64	*5.18*	1.70	-	8.90	*9.67*	3.10	*2.73*	8.6
Paranaiba	L6	4.8	7.98	745	71	2.57	580	*493*	99	59.2	*50.7*	6.01	*5.87*	1.53	-	9.12	*11.2*	1.92	*2.27*	8.9
Ramsdorf[3]	L6	1.7	9.03	721	79	2.77	323	*356*	76	≤6.4	*1.3*	3.19	*2.80*	1.41	-	7.33	*8.34*	2.64	*2.60*	9.5
Segowlie	L6	1.7	8.56	665	67	2.66	566	*450*	99	58.2	*56.0*	5.34	*5.38*	1.44	-	10.1	*9.49*	2.84	*2.86*	9.3
Tathlith[3]	L6	2.0	8.32	711	69	2.64	615	*505*	104	71.1	*70.1*	5.49	*5.70*	1.71	-	9.60	*8.26*	2.19	*3.20*	8.5
Tourinnes-la-Grosse[3]	L6	1.6	8.42	679	70	2.63	596	*638*	103	74.7	*33.7*	5.52	*3.92*	1.55	*1.4*	9.82	*9.06*	2.23	*1.69*	8.7
Tuan Tuc[3]	L6	1.7	8.64	707	74	2.69	508	*559*	92	47.5	*41.1*	5.35	*5.87*	1.47	*1.3*	7.88	-	2.04	*1.56*	9.0
Utrecht	L6	1.6	7.48	567	57	2.59	734	*912*	98	129	*115*	4.86	*4.71*	1.58	-	9.17	*11.1*	2.17	*2.25*	8.3
Valdinizza	L6	1.6	8.56	677	77	2.72	517	*325*	95	61.4	*43.9*	5.74	*5.31*	1.68	-	7.26	*6.83*	3.34	*2.31*	8.9
Vouillé[3]	L6	1.8	8.53	678	72	2.68	558	*491*	112	61.0	*45.9*	5.59	*4.89*	1.47	*0.9*	12.1	-	2.52	*2.25*	8.9
Wethersfield (1971)[2]	L6	1.7	8.52	689	70	2.65	594	*613*	117	63.0	*48.8*	5.59	*5.05*	1.56	-	11.3	*11.8*	2.39	*2.3*	9.0
Wethersfield (1982)	L6	1.6	8.53	646	69	2.63	530	*614*	100	60.2	*73.2*	5.40	*5.38*	1.41	-	10.5	*9.90*	2.47	*2.04*	8.4

[a] Data in normal type from ICPMS; data in italics from RNAA. *RNAA* data from: 1. Binz *et al.* (1976); 2. Huston and Lipschutz (1984); 3. Neal *et al.* (1981); 4. Walsh and Lipschutz (1982). ICPMS data represent 3 replicates except 2 replicates for Elenovka and Tathlith (see text).

Suspicious data are in parentheses.

schutz and Samuels, 1991; Wolf and Lipschutz 1995b), we use LDA and LR for these compositional comparisons. Conceptually, the simpler technique is LDA which uses a standard linear regression model to obtain multivariate discriminant functions and assumes an equally distributed covariance matrix (i.e., equal probability of membership in one of two groups). When using LDA, we also assume normal multivariate distributions. The other technique, LR, shares many principles of LDA but LR is less sensitive to the actual distribution function of the multivariate data (Wolf and Lipschutz, 1995b, and references therein). The LR method also assumes equal probability of membership in one of two groups.

These standard LDA and LR techniques are model-dependent, relying on a specific distribution function assumption to describe independent variables (i.e., they assume that elemental distributions of L chondrites can be described by a normal curve rather than a Poisson, lognormal, or other distribution). A possible complication when the shape of the distribution functions are not normal is to reflect bias in statistical results. One technique to reduce the likelihood of this model-dependent bias uses a Monte Carlo–like method to simulate random noise in a data set's distribution(s) and compensate for potentially unrepresentative data. Lipschutz and Samuels (1991) developed such a model-independent method, randomization-simulation, which uses the metrics of standard LDA or LR to test for chance effects. In this technique, new data sets are generated by randomly assigning meteorites to, in our case, one of two sample suites nominally classified by a petrographic parameter (e.g., L5 and L6 or mildly and strongly shocked). Randomly generated suites must be of the same size as those displayed by the actual data. Each pair of randomly generated suites, with their associated compositional data, is then compared using the metric of either LDA or LR. Following generation of some number of random, simulated data sets, we calculate a model-independent *p*-value simply by observing the number of randomly generated sets which do as well as or better than the actual data in classifying the suites (i.e., which have as few as or fewer misclassifications than in the actual case).

As will be seen, for a variety of reasons, a few of our data seem suspicious. Since our statistical techniques require a numerical entry for every datum, we replaced each suspicious value (i.e., the parenthetical ones) in Table 2 with the mean concentration of that element in all remaining L4-6 (S1–S6) chondrites. Additionally, due to changes in the RNAA analytical suite over time, some meteorite-element data do not exist: here too, we use the mean of that element calculated from all samples in statistical treatments (e.g., Cd is represented by a mean 12 times). This conservative action makes the task of computational clas-

Table 2b. Trace element results for L chondrites (Z = 39–60).[a]

Meteorite	Y (μg/g)	Zr (μg/g)	Nb (ng/g)	Mo (μg/g)	Ru (μg/g)	Pd (ng/g)	Ag (ng/g)	Cd (ng/g)	In (ng/g)	Sn (μg/g)	Sb (ng/g)		Te (ng/g)		Cs (ng/g)		Ba (μg/g)	La (ng/g)	Ce (ng/g)	Pr (ng/g)	Nd (ng/g)
Atarra	2.55	8.0	—	3.0	1.5	634	*83.1*	*68.1*	*0.71 ± 0.67*	0.89	140	*110*	356	*248*	223	*246*	5.12	1290	2300	273	1020
Bald Mountain[3]	2.50	7.4	—	2.5	1.4	451	*62.2*	—	*1.1*	1.8	84	*89*	412	*367*	82.4	*64.2*	3.53	449	1010	152	697
Rio Negro	2.36	7.7	—	2.3	1.3	455	*105*	*165*	*10.0*	4.6	82	*88*	451	*270*	249	*225*	4.03	1110	1280	143	649
Saratov[2]	2.52	7.7		2.0	1.4	749	*33.5*	*58*	*7.0*	1.7	68	*300*	380	*395*	181	*110*	8.72	378	952	145	677
Tennasilm[1]	2.34	7.2	490	1.6	1.4	611	—	—	*14.8*	0.88	180	*102*	1090	*380*	295	—	3.09	323	851	131	618
Ausson[3]	2.33	7.5	—	1.9	1.3	517	*93.7*	—	*1.60*	0.42	79	*(2300)*	474	*521*	34.7	*16.1*	3.37	368	856	131	610
Baszkówka	2.45	7.5	480	1.6	1.2	601	*78.5*	*35.9*	*3.69*	3.9	59	*40*	522	*381*	147	*141*	3.21	338	901	137	632
Crumlin[3]	2.21	7.5	—	2.4	1.3	567	*47.9*	—	*0.5*	(13)	270	*180*	461	*405*	50.6	*34.5*	3.38	344	820	125	586
Elenovka[3]	2.29	7.9	—	2.0	1.3	619	*67.7*	—	*3.10*	0.28	38	*85*	424	*405*	12.4	*16.2*	3.68	429	935	138	638
Farmington[4]	2.49	7.1	450	1.7	1.5	558	*32.5*	*0.47*	*0.67*	0.34	64	—	685	*345*	5.11	*7.36*	3.09	349	927	140	656
Guibga	2.33	7.3	—	2.1	1.4	730	*44.4*	*25.9*	*≤0.73*	0.37	77	*72*	497	*257*	10.7	*11.8*	3.08	336	824	128	593
Homestead	2.41	7.1	520	2.6	1.3	496	*28.4*	*26.1*	*0.23 ± 0.19*	0.73	76	*180*	429	*346*	51.0	*52.3*	3.38	320	858	133	624
Honolulu	2.03	6.9	460	1.6	1.4	751	*51.7*	*23.2*	*0.17 ± 0.16*	0.87	70	*120*	492	*313*	25.2	*42.2*	3.20	282	731	114	534
Innisfree	2.30	7.0	480	1.5	1.3	716	*50.4*	*28.6*	*≤0.29*	0.31	89	*72*	1140	*1530*	131	*123*	3.03	318	838	129	604
Jhung[3]	2.54	7.6	—	2.0	1.4	294	*336*	—	*1.20*	0.95	85	*85*	400	*332*	3.01	*12.5*	3.31	423	956	145	673
Malakal[4]	2.41	7.9	—	2.0	1.3	669	*26.9*	*17.3*	*0.23*	0.52	89	—	425	*394*	30.6	*27.6*	3.88	(1270)	918	138	638
Monte das Fortes	2.07	5.7	390	1.4	1.5	950	*65.7*	*4.48*	*0.17 ± 0.16*	0.58	130	*99*	751	*346*	21.1	*23.4*	3.28	337	870	130	592
Shelburne	2.22	7.1	520	1.4	1.3	462	*29.2*	*11.7*	*≤0.52*	1.5	52	*49*	396	*296*	19.6	*17.8*	3.26	312	839	127	592
Tané	2.42	7.1	460	1.4	1.3	791	*23.8*	*5.21*	*0.30 ± 0.17*	0.97	65	*97*	238	*321*	3.00	*3.51*	3.00	326	870	134	632
Apt[3]	2.27	7.4	—	1.9	1.3	886	*110*	—	*0.50 ± 0.10*	0.50	1000	*410*	455	*392*	5.13	*12.1*	3.67	431	832	126	580
Aumale[3]	2.32	7.6	—	1.8	1.2	556	*114*	—	*0.80*	0.49	72	*120*	462	*378*	10.5	*8.77*	4.30	(887)	868	130	607
Bruderheim[4]	1.94	6.9	470	1.7	1.4	770	*80.6*	*4.36*	*≤0.64*	0.64	75	—	450	*331*	4.16	*8.75*	3.23	295	752	114	520
Chantonnay[3]	2.61	7.7	—	2.4	1.2	813	*60.5*	—	*0.40 ± 0.05*	0.41	82	*66*	420	*394*	3.50	*28.4*	3.68	(666)	993	152	693
Denver	2.72	8.2	—	2.1	1.1	459	*57.9*	*29.6*	*≤0.46*	0.79	69	*56*	455	*341*	6.70	*82.5*	3.90	397	1010	151	708
Girgenti	2.45	7.1	—	1.8	1.3	709	*171*	*386*	*≤0.76*	0.34	82	*54*	435	*274*	2.73	*2.24*	3.50	369	878	136	633
Karkh	2.38	7.3		2.0	1.2	612	*89.8*	*22.9*	*0.59 ± 0.19*	0.55	61	*57*	460	*428*	10.6	*6.44*	3.63	351	874	132	621
Kunashak	2.37	7.1	480	1.7	1.3	612	*67.8*	*7.27*	*≤0.43*	0.33	110	*120*	300	*241*	8.59	*5.29*	3.70	360	920	139	627
Kuttippuram[4]	2.28	8.5	—	3.9	1.5	820	*438*	*122*	*1.24*	0.68	110	—	429	*378*	40.7	*55.6*	7.93	317	831	126	597
Kyushu	2.54	7.8	550	1.7	1.3	469	*91.5*	*15.2*	*0.21 ± 0.16*	0.41	90	*39*	378	*381*	3.60	*5.02*	3.39	350	937	142	674
La Criolla	2.46	7.4	470	1.4	1.1	509	*46.6*	*1.32*	*≤0.46*	0.32	62	*37*	481	*265*	30.9	*26.5*	3.23	353	925	140	650
L'Aigle[3]	2.33	7.5	—	1.8	1.3	746	*74.6*	—	*≤0.60*	0.29	66	*75*	483	*444*	4.59	—	3.06	336	798	124	580
Leedey	2.34	8.6	—	2.7	1.6	883	*116*	*24.4*	*0.28 ± 0.24*	1.2	170	*160*	473	*210*	2.77	*4.61*	3.73	364	850	130	597
Louisville dark	2.13	7.7	—	2.6	1.3	719	—	—	—	0.30	89	—	420	—	6.59	—	3.19	(533)	785	119	550
Louisville light[2]	2.36	8.0	—	2.1	1.2	641	*48.7*	*81*	*≤0.07*	0.36	160	—	442	*267*	5.21	*3.41*	3.22	(612)	857	130	597
Modoc (1905)	2.40	8.9	510	1.7	1.3	509	*42.8*	*124*	*0.75 ± 0.22*	0.39	74	*37*	449	*225*	70.7	*59.5*	3.75	371	954	140	648
Nejo	2.35	7.4	—	2.4	1.3	588	*202*	*875*	*≤0.37*	1.8	130	*79*	383	*371*	4.30	*3.94*	3.82	(739)	1040	148	660
New Concord	2.21	6.9	500	2.1	1.4	519	*31.8*	*57.8*	*≤0.28*	3.0	160	*27*	467	*430*	13.5	*2.18*	3.34	318	824	127	587
Paranaiba	2.45	8.7	—	3.1	1.2	589	*991*	*53.9*	*0.62 ± 0.14*	0.59	97	*71*	550	*419*	7.08	*17.5*	9.77	(8270)	1000	149	673
Ramsdorf[3]	2.46	7.6	510	1.1	0.8	442	*43.4*	*0.5*	*0.85*	0.030	260	—	415	*334*	61.4	*85.1*	3.37	344	912	139	645
Segowlie	2.32	7.4	—	2.1	1.2	667	*(1280)*	*177*	*0.53 ± 0.21*	1.9	57	*48*	450	*227*	12.1	*9.47*	3.24	414	856	130	598
Tathlith[3]	2.25	9.1	—	2.5	1.4	609	*123*	*147*	*2.56*	0.46	51	—	337	*268*	13.6	*21.3*	4.05	406	964	136	622
Tourinnes-la-Grosse[3]	2.35	7.8	—	2.0	1.3	672	*62.4*	*7.91*	*0.80*	0.45	110	*840*	390	*296*	3.27	*5.7*	3.53	340	856	130	611
Tuan Tuc[3]	2.58	8.3	—	1.9	1.3	663	*82.4*	—	*≤0.20*	0.28	81	*100*	286	*254*	5.45	*6.43*	4.07	452	968	147	684
Utrecht	2.28	6.3	470	1.7	1.4	649	*34.9*	*2.24*	*0.28*	0.31	110	*110*	687	*551*	12.1	*14.3*	3.06	337	884	136	622
Valdinizza	2.16	7.4	—	1.5	1.3	637	*227*	*40.4*	*0.41*	0.47	59	*43*	520	*292*	4.26	*3.87*	3.38	303	822	119	550
Vouillé[3]	2.46	7.9	—	2.2	1.2	592	*136*	—	*0.70*	0.51	220	*300*	469	*401*	3.49	*3.1*	3.27	(624)	933	142	665
Wethersfield (1971)[2]	2.63	8.3	—	2.3	1.3	434	*49.6*	*44*	*≤0.04*	0.66	76	—	354	*379*	3.59	*4.02*	3.47	397	1020	154	706
Wethersfield (1982)	2.25	7.5	450	1.4	1.2	573	*542*	*36.9*	*≤0.33*	0.30	60	*95*	493	*372*	2.37	*10*	3.10	301	805	123	582

[a] Data in normal type from ICPMS; data in italics from RNAA. *RNAA* data from: 1. Binz *et al.* (1976); 2. Huston and Lipschutz (1984); 3. Neal *et al.* (1981); 4. Walsh and Lipschutz (1982). ICPMS data represent 3 replicates except 2 replicates for Elenovka and Tathlith (see text).

Suspicious data are in parentheses.

sification of each selected suite even more rigorous since the metric must rely more heavily on relationships among other elements, while still using that element as an input for other samples. Replacing data with some other value (e.g., L5 only, L6 only, or S3 only) would have introduced bias into our calculations. For cases in which we list only an upper limit, we use that limit as the concentration in our computations. Finally, since W contamination was serious for many samples (see below) and, as a result, many Nb values are missing, we omitted these 2 elements from our computations, leaving us with data for 49 elements. Wolf and Lipschutz (1995b) found bias between different RNAA analysts minimal compared to natural variations of thermally labile elements. Nonetheless, to further reduce any possible method or analyst bias in our calculations, we use the average of ICPMS and RNAA data in the cases when data exist for the same element (see next section).

3. RESULTS

In Table 2 we list the compositional data for our suite of 48 L chondrite falls. For completeness, we include RNAA data previously reported (cf. Table 1) for 22 of these 48 samples. As noted above, missing values reflect changes in the RNAA element suite over time.

Many Smithsonian Meteorite Powder Collection samples were homogenized at the Smithsonian Institution in a tungsten carbide grinding apparatus. These samples proved to be W-contaminated: for them and others unknowingly analyzed in the same ICPMS runs, we omit both W and Nb data since W^{2+} overlaps Nb^{+}. We find no evidence for contamination by any other element in samples processed in tungsten carbide.

An unnamed reviewer noted that while RNAA is a well-established analytical method for meteorite analyses, ICPMS has not been recognized to be competitive to RNAA. In fact, this is not the case today. In reviewing applications of all analytical techniques to geochemistry and cosmochemistry in 1997–1999, Lipschutz et al. (1999) noted that ICPMS was already a significant tool for geochemical analyses of many elements at levels similar to those in meteorites. Subsequently, ICPMS has displaced many techniques used for geochemical

Table 2c. Trace element results for L chondrites (Z = 62–92).[a]

Meteorite	Sm (ng/g)	Eu (ng/g)	Gd (ng/g)	Tb (ng/g)	Dy (ng/g)	Ho (ng/g)	Er (ng/g)	Tm (ng/g)	Yb (ng/g)	Lu (ng/g)	Hf (ng/g)	W (ng/g)	Re (ng/g)	Ir (ng/g)	Pt (μg/g)	Au (ng/g)	Tl (ng/g)	Bi (ng/g)	Th (ng/g)	U (ng/g)
Atarra	222	81	339	63	323	81.5	240	39	228	43	205	—	68	588	1.1	*157*	*1.23*	*4.68*	49	18.0
Bald Mountain[3]	237	78	308	61	318	79.9	232	39	228	42	180	—	68	583	1.1	*190*	*9.03*	*4.93*	46	13.1
Rio Negro	220	76	293	57	296	75.5	220	37	219	40	194	—	56	491	0.93	*54.0*	*20.8*	*31.1*	55	32.9
Saratov[2]	233	84	312	62	319	82.4	238	39	236	43	187	—	81	763	1.2	*171*	*0.94*	*7.49*	51	17.0
Tennasilm[1]	215	81	304	59	309	76.4	227	39	229	41	173	324	63	586	1.0	*220*	*6.3*	*7.75*	50	12.7
Ausson[3]	210	76	280	55	291	74.1	220	36	215	40	181	—	65	572	1.0	*190*	*3.02*	*13.4*	49	20.5
Baszkówka	219	78	290	58	305	79.0	230	37	222	42	178	—	59	562	0.94	*147*	*2.60*	*16.2*	49	10.2
Crumlin[3]	200	79	266	54	282	70.2	206	35	209	38	185	—	62	559	1.0	*170*	*0.83*	*4.48*	47	16.6
Elenovka[3]	214	78	292	56	303	73.9	222	37	223	39	196	—	63	564	0.99	*180*	*6.29*	*7.48*	60	15.7
Farmington[4]	231	79	308	60	324	80.0	237	40	235	42	169	158	66	616	1.2	*157*	*0.23*	*0.23*	49	12.7
Guibga	206	78	286	55	295	75.7	218	37	209	40	171	—	61	570	1.1	*91.0*	*1.07*	*2.63*	45	13.0
Homestead	222	79	298	58	307	77.7	224	38	224	41	167	—	59	593	1.0	*160*	*1.78*	*11.6*	55	13.3
Honolulu	187	76	251	50	261	65.4	194	33	198	37	161	—	64	602	1.0	*148*	*3.02*	*1.64*	42	8.60
Innisfree	214	78	282	56	293	73.5	218	37	218	39	163	111	62	562	1.0	*99.0*	*2.71*	*0.54*	45	10.9
Jhung[3]	236	81	314	61	322	81.0	237	39	236	44	188	—	65	588	1.1	*175*	*2.37*	*9.72*	49	16.9
Malakal[4]	221	82	299	58	305	76.2	228	38	222	41	190	—	64	592	1.0	*176*	*0.07*	*1.32*	52	19.8
Monte das Fortes	200	84	274	52	274	69.1	194	33	201	35	146	—	76	717	1.3	*185*	*2.36*	*0.33*	49	26.8
Shelburne	210	78	280	55	288	72.7	213	36	210	39	167	—	61	559	1.0	*126*	*0.75*	*0.97*	47	14.8
Tané	223	75	285	58	301	75.8	228	38	224	41	169	—	62	528	0.97	*167*	*0.55*	*4.77*	47	8.20
Apt[3]	202	81	277	53	284	71.9	212	35	211	40	178	—	71	616	1.1	*200*	*4.44*	*5.02*	51	19.8
Aumale[3]	212	84	285	55	292	74.1	215	37	216	41	179	—	60	572	0.97	*120*	*1.50*	*5.88*	52	12.6
Bruderheim[4]	171	76	239	48	248	62.5	184	32	193	36	165	232	67	654	1.2	*290*	*0.32*	*0.89*	68	14.5
Chantonnay[3]	240	83	315	62	326	82.6	244	40	234	44	187	—	60	540	1.0	*150*	*1.31*	*9.03*	53	17.1
Denver	248	83	326	63	336	85.3	251	42	237	45	201	—	54	502	0.95	*265*	*10.0*	*3.87*	51	16.1
Girgenti	217	78	296	57	301	78.1	231	37	220	41	163	—	61	548	1.0	*120*	*2.86*	*3.47*	46	25.6
Karkh	214	77	288	56	303	74.4	222	37	213	40	175	—	60	577	1.1	*157*	*1.37*	*2.67*	49	9.40
Kunashak	222	82	292	58	302	76.5	221	38	224	41	165	—	61	582	1.0	*152*	*0.50*	*3.15*	52	17.5
Kuttippuram[4]	203	80	273	53	277	71.0	210	35	204	38	227	—	82	642	1.2	*188*	*5.46*	*18.1*	47	24.3
Kyushu	232	83	314	62	327	81.4	237	39	231	43	176	—	58	548	0.93	*154*	*1.45*	*1.69*	44	12.6
La Criolla	224	83	304	59	317	78.7	225	38	226	41	175	—	54	521	0.89	*109*	*0.13*	*0.32*	48	11.4
L'Aigle[3]	202	78	285	55	292	73.5	214	36	210	39	179	—	56	588	1.1	*110*	*0.40*	*8.69*	47	13.2
Leedey	207	78	284	55	294	72.5	218	36	216	40	214	—	80	718	1.4	*(3310)*	*16.2*	*6.90*	49	27.8
Louisville dark	190	76	247	50	263	66.8	197	34	201	38	190	—	73	653	1.2	—	—	—	47	17.1
Louisville light[2]	211	78	272	54	290	73.9	217	37	221	41	194	—	60	532	0.98	*120*	*0.03*	*2.15*	47	15.3
Modoc (1905)	217	82	294	58	306	76.6	223	38	221	41	204	—	58	548	0.92	*28.0*	*0.99*	*2.04*	(190)	29.2
Nejo	212	78	292	58	298	73.8	221	37	217	40	174	—	60	588	1.0	*144*	*8.82*	*2.67*	51	18.2
New Concord	202	78	277	54	286	71.7	204	35	212	38	165	—	59	552	0.98	*119*	*0.22*	*2.07*	56	24.7
Paranaiba	222	79	303	59	308	75.7	223	39	220	40	218	—	61	529	0.92	*229*	*2.96*	*8.91*	50	12.7
Ramsdorf[3]	223	87	309	61	315	81.3	236	41	239	42	181	90	37	376	0.64	*107*	*≤0.14*	*0.09*	53	16.0
Segowlie	208	76	279	55	299	75.3	217	38	222	40	181	—	51	492	0.86	*36.0*	*16.2*	*23.6*	43	34.7
Tathlith[3]	207	75	285	54	295	71.6	215	37	215	38	222	—	61	572	1.1	*163*	*1.46*	*12.6*	51	20.5
Tourinnes-la-Grosse[3]	215	78	276	55	294	74.8	221	37	223	41	192	—	65	578	1.1	*241*	*2.86*	*6.99*	46	19.7
Tuan Tuc[3]	238	84	305	61	324	82.0	241	41	238	44	199	—	66	604	1.2	*160*	*5.25*	*6.70*	47	16.7
Utrecht	219	76	288	55	298	74.0	217	37	221	40	148	195	64	612	1.1	*216*	*0.84*	*1.58*	58	16.4
Valdinizza	199	82	265	53	282	69.7	206	36	212	39	176	—	61	585	1.1	*129*	*0.87*	*1.28*	42	11.6
Vouillé[3]	228	80	304	60	313	78.0	231	39	226	42	196	—	59	565	0.99	*130*	*4.25*	*21.5*	49	13.1
Wethersfield (1971)[2]	245	83	332	64	340	83.5	247	40	234	43	203	—	62	544	1.2	*148*	*≤0.03*	*0.78*	55	19.6
Wethersfield (1982)	204	78	270	54	287	72.2	212	36	215	40	177	—	58	572	0.99	*197*	*4.69*	*3.65*	43	8.50

[a] Data in normal type from ICPMS; data in italics from RNAA. *RNAA* data from: 1. Binz *et al.* (1976); 2. Huston and Lipschutz (1984); 3. Neal *et al.* (1981); 4. Walsh and Lipschutz (1982). ICPMS data represent 3 replicates except 2 replicates for Elenovka and Tathlith (see text).

Suspicious data are in parentheses.

elemental analysis (Lipschutz et al., 2001, 2003) so that NAA techniques may be considered obsolescent for all but perhaps the most volatile elements. This revolution has not yet taken place in cosmochemical research for reasons, we suspect, other than the general quality of ICPMS data. The quality of our ICPMS data for C1-3 and L4-6 chondrites has been demonstrated for the 8 elements for which comparison with RNAA data is possible (Friedrich et al., 2002, 2003). Only Cs and Te data seem discrepant but the conclusions of those studies (and this one) are identical whether one relies upon only the RNAA or ICPMS data, or their mean for the 8 elements in common (Friedrich et al., 2002, 2003).

We use parentheses in Table 2 to identify 12 suspicious data. These are generally several orders of magnitude higher than results for the same element in other L4-6 chondrites and may reflect sampling or contamination effects. Suspicious lanthanum data are the most troubling. Atarra, Rio Negro, Malakal, Aumale, Chantonnay, Louisville light and dark, Nejo, Paranaiba, and Vouille are each enriched by at least 2× the average L chondrite value. For Atarra, one of only 5 L4 samples in our suite, the enrichment might be attributed to mineralogical heterogeneity (Friedrich et al., 2003). Rio Negro is a regolith breccia and is seemingly rich in many lithophiles. (In earlier RNAA studies, Lipschutz et al. (1983) noted high contents of Rb and Cs in H chondrite regolith breccias.) While we exclude Atarra and Rio Negro from our statistical calculations, we do not consider their La data as suspicious. No reasonable ICPMS oxide or hydroxide interference on ^{139}La can be responsible for these La enrichments. Is it only coincidence that 7 of the remaining 8 L5 and L6 chondrites with suspiciously high La contents are highly shocked (S4-S6)? Since our samples are observed falls, terrestrial contamination by La seems unlikely. However, Crozaz et al. (2003) report LREE contamination (sometimes only La) in meteorites from hot and cold deserts. These enrichments are particularly evident in highly shocked individuals with an extensive network of microfractures and cracks, hence large surface areas (Floss, personal communication). It is possible that freshly collected falls with 30–200 yr terrestrial ages could also be enriched in La either through a similar process or through cross-contamination of meteorites during curatorial handling and storage.

Detailed discussion of the demonstrated precision and accuracy of our ICPMS technique is presented elsewhere (Friedrich et al., 2002, 2003) and it is sufficient to point out that 41 of 45 elements show intrasample precision better than 10%, with 30 of 45 being better than 5%. If, for the moment, we ignore the 9 elements that we determined by both ICPMS and RNAA, prior results exist for $<$10% of our 2664 meteorite-element data (Table 2), so that only limited comparison is possible. Of the 400 prior data (Koblitz, 2003), 247 (62%) agree with ours to $\leq$15% and an additional 39 (10%) agree with ours to within 20%. The remaining 114 data differ by $>$20%. As Friedrich et al. (2003) discussed, the majority of differences generally involve the most thermally labile elements (e.g., Co, Ga, Rb, Cs, Se, Ag, Te, Zn, In, Bi, Tl, Cd in order of ease of loss from chondrites during heating at 1000°C) or are chemically ill behaved (e.g., As, Sb) during sample preparation, or both. Comparisons involving data from this study yield similar trends: almost half (54 of 114) of our results and prior ones discordant at $>$20% involve this suite of elements. Many prior data by us and others disagree by 1–2 orders of magnitude even when different chips of the same ordinary chondrite were analyzed by the same investigator in the same study.

When considering the more refractory elements, only a handful vary by more than 30% from prior data. Our Rio Negro Li value is 2.4× the thermal NAA value of Quijano-Rico and Wänke (1969) while our Saratov datum is 44% lower than that of Murty et al. (1983). For Sc, Ti, V, Mn, and Cu, 10 values differ by $>$30% from literature data. Prior Zr data exist for 9 of our samples: 7 agree to within 25% but our Farmington and Kunashak results are, respectively, 31% lower and 65% higher than prior XRF (Michaelis et al., 1969) or NAA (Ehmann and Rebagay, 1970) data. There are surprisingly few prior REE data for the 48 L4-6 chondrites considered here: in 50 of the 59 cases, our data and prior ones agree within 20%. For Ir, 9 of 20 values agree within $<$15% and 4 others, within 20%: 7 disagree by $>$30%. The only case of a systematic difference involving siderophiles is Bruderheim, where our Pd, Pt, and Au data are each higher than literature means by at least 30%; however, our Bruderheim La datum is only 5% higher than that of Haas and Haskins (1991), which should be particularly accurate. This suggests that sampling heterogeneity in Bruderheim is not a significant problem.

The 9 elements for which we report both ICPMS and RNAA data (Table 2) are thermally labile to a greater or lesser degree and, traditionally, only factors-of-two differences in their contents are taken to signal possible disagreements even between aliquots in all but carbonaceous chondrites (Lipschutz and Woolum, 1988; Palme et al., 1988). In comparing the data for Co, Zn, Ga, As, Se, Rb, Sb, Te and Cs, the percentage of differences for each element vary somewhat, from the absence of any disagreements for Ga, Se and Rb in 47, 36 and 46 samples, respectively, to ~20% disagreements each for Sb and Cs—7 of 39 and 9 of 45 samples, respectively. The remaining elements—As, Co, Zn and Te—reveal 1 of 14, 2 of 47, 2 of 46 and 3 of 47 samples, respectively that disagree by $>$2× (Table 2).

When considering only the 39 Smithsonian Meteorite Powder Collection sample aliquots that were analyzed by both methods specifically for this study (Table 1), comparisons are as favorable as those in Friedrich et al. (2002, 2003). Within this group, the quantity of RNAA and ICPMS values agreeing to within 20% of each other are: Ga (95%), Se (80%), and Cs (67%). Six other elements (Co, Zn, Rb, Sb, Te) all have between 44 and 50% of values agreeing to within 20%. Of the remaining, more discrepant, values it is interesting to note that in each case (except Rb with two each) the strongly shocked samples have twice the number of discrepant values, which indicates that chemical and mineralogical heterogeneity is likely a factor when sampling even homogenized meteorite powders for chemical analysis. For As, all but one ICPMS datum are higher than those obtained by RNAA: the other 8 elements do not exhibit this pronounced systematic difference although many ICPMS values in this suite are higher than their corresponding RNAA datum. Considering the normally variable contents of these 9 elements in L (and other) chondrites and the absence of any objective reason to view any of these data with more than the usual intratechnique suspicion, we assume that all of these data are valid. In the discussion that follows, we chose to adopt only the ICPMS As values because of the paucity of RNAA As data and the hint of a systematic difference between them. In the case of the other 8 elements, we used the mean of the ICPMS and RNAA data for graphical and statistical analyses of each member of the 48 L4-6 chondrites in our suite. Our observations and conclusions to be discussed would be identical if either the ICPMS or RNAA were used instead of their mean (Friedrich, 2002; Friedrich et al., 2002, 2003).

Table 3. Comparison by petrographic type of our suite with the total population known.[a]

	This work	Falls	All
L4	5	20	415
L5	14	61	1220
L6	28	239	4053
Total	47	320	5688

[a] Data from Grady (2000).

4. DISCUSSION

For our purposes, it is not essential or even important that our sample suite be representative of the current population of L chondrites falls but, in fact, differences are not great. As can be seen from Table 3, our sample suite contains a higher percentage of L5s than is found among falls or falls and finds together, 30% vs. 19 or 21%, respectively, and a concomitant deficit of L6s, 60% vs. 75 or 71%, respectively (Table 3). We place greater reliance upon data for falls since finds include Antarctic individuals, thus raising the pairing question addressed elsewhere (cf. Wolf and Lipschutz, 1995a).

With respect to shock stage (Table 4), our sample suite compared with all falls is deficient in chondrites of S2, 4% vs. 16%, respectively, and concomitantly richer in S4 samples, 47% vs. 29%, respectively. As a result, our sampling of mildly shocked (S1-S3) and highly shocked (S4-S6) L4-6 chondrites, 45% vs. 55%, respectively, approximates a mirror image of the distribution among all falls, 55% vs. 45%, respectively (Table

Table 4. Comparison by shock stage for our L4-6 suite with known shock-classified L4-6 population.[a]

	This work	Falls	All
S1	1	3	76
S2	2	17	316
S3	18	40	567
S4	22	32	514
S5	3	14	137
S6	1	3	90
Total	47	109	1700

[a] Data from Koblitz (2003).

4). It should be noted that data for many samples in our suite—particularly for petrographic type (Table 3)—are included in the numbers for all falls.

4.1. Effects of Petrographic Type on Elemental Patterns

To assess the extent to which the chemical composition of equilibrated falls varies with petrographic type—i.e., during metamorphism of their parent(s)—we must consider only mildly shocked (S1-S3) chondrites. This essentially limits us to comparison of L5 with L6 chondrites (which we represent in Fig. 1 as L6/L5 ratio) since the number of L4 chondrites is small, 5, and of these, Atarra and Rio Negro present unusual compositional aspects as noted earlier. The subsets then include 9 L5 (Ausson, Baszkówka, Elenovka, Guibga, Honolulu, Innisfree, Jhung, Monte das Fortes, Tané) and 8 L6 (Kuttippuram, L'Aigle, Nejo, Segowlie, Tathlith, Tourinnes-la-Grosse, Utrecht, Wethersfield 1982) chondrites.

For simplicity, we divide our elemental suite into four subgroups, each ordered by increasing thermal lability (Fig. 1): 24 refractory lithophiles (in order of increasing putative volatility: Hf, Lu, Zr, Y, Ti, Sc, Er, Th, Ho, Tm, Dy, Tb, Gd, U, Nd, Pr, Sm, La, Ce, V, Yb, Eu, Sr, Ba), hereafter Hf-Ba; 8 siderophiles (in decreasing condensation temperature: Re, Ir, Mo, Ru, Pt, Co, Pd, Au), hereafter Re-Au; 6 moderately volatile elements (Li, Mn, As, Cu, Sb, Sn), hereafter Li-Sn; and 11 highly volatile or -mobile trace elements (in order of increasing thermal lability: Ga, Rb, Cs, Se, Ag, Te, Zn, In, Bi, Tl, Cd), hereafter Ga-Cd. Means discussed for each element of the first three subgroups are arithmetic: because of the well-established, greater variability of highly mobile elements, the mean for each of these 11 is geometric.

For the 24 refractory lithophiles, Hf-Ba, most mean L6/L5 ratios are at or near unity, with U and Ba lying above this by 37 and 22% respectively (Fig. 1). The U and Ba discrepancies

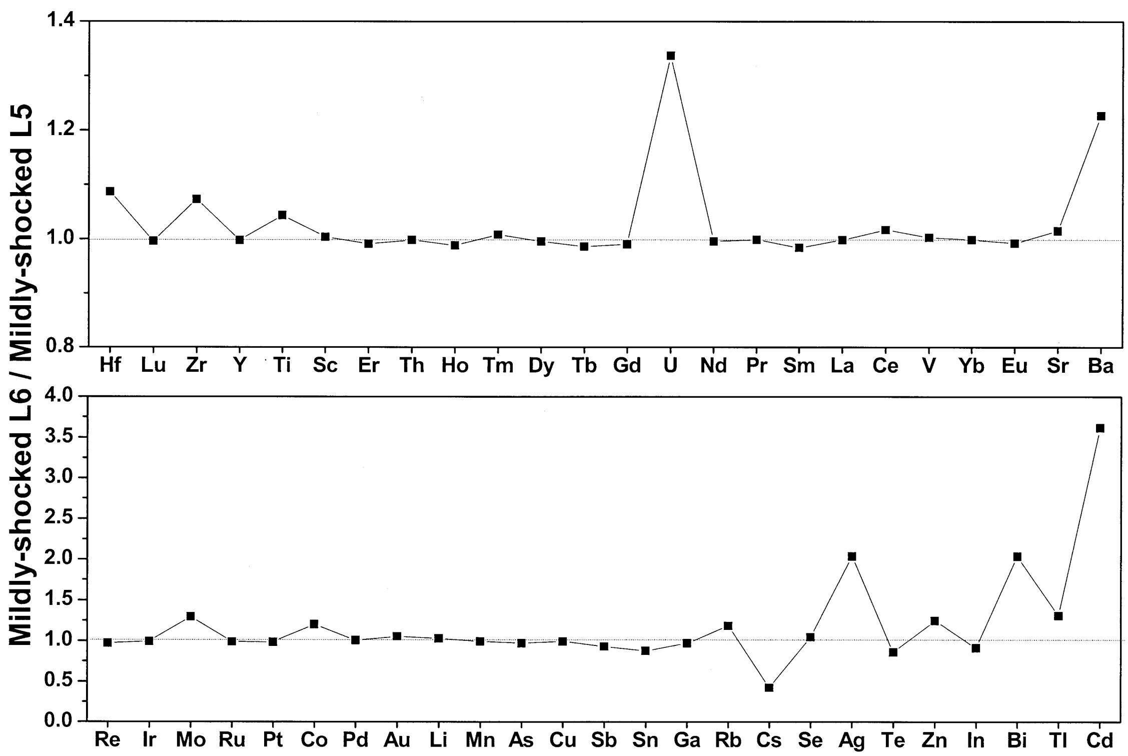

Fig. 1. Mildly shocked L6 chondrite mean (n = 8) normalized to mildly shocked L5 chondrite mean (n = 9) for 24 refractory lithophiles and 25 refractory siderophiles and moderately to highly volatile elements. Deviations of some elements (e.g., U, Ba, Mo, Cs, Ag, Bi, Cd) are due to single extreme, but analytically valid, individual sample values. Lithophiles (Hf-Ba, n = 24), on average, show little deviation from unity (1.02 ± 0.07). When the two most variable lithophiles (U, Ba) are ignored the mean and associated standard deviation becomes 1.01 ± 0.03. Treating 8 refractory siderophiles (Re-Au, n = 8) yields 1.06 ± 0.13 (1.00 ± 0.05 ignoring Mo). Six moderately volatile elements (Li-Sn) demonstrate a mean and standard deviation of 0.96 ± 0.05. Highly volatile and thermally labile elements (Ga-Cd, n = 11) are generally more variable, but when the most variable, Cd, is ignored, the ratio, 1.10 ± 0.45, demonstrates little variation from unity.

Table 5. Weight normalized means and 1σ errors of elemental suites for L chondrites in this study.

	Lithophiles (Hf-Ba, n = 24)	Siderophiles (Re-Au, n = 8)	Moderately Volatile (Li-Sn, n = 6)	Volatile/Labile (Ga-Cd, n = 11)[a]
L6 mildly (n = 8)/L5 (n = 9) mildly shocked	1.02 ± 0.07	1.06 ± 0.13	0.96 ± 0.05	1.23 ± 0.56
L4-6 strongly (n = 26)/mildly (n = 19) shocked	1.03 ± 0.01	0.95 ± 0.05	0.97 ± 0.11	0.68 ± 0.37
L5 strongly (n = 5)/mildly (n = 9) shocked	1.02 ± 0.02	1.00 ± 0.09	0.98 ± 0.04	0.66 ± 0.52
L6 strongly (n = 20)/mildly (n = 8) shocked	1.03 ± 0.04	0.93 ± 0.07	0.99 ± 0.11	0.66 ± 0.44

[a] Geometric mean and standard deviation of individual element geometric means.

each reflect one aberrant point, for Segowlie and Kuttippuram, respectively (Table 2): omitting these 2 data, the overall mean for the 24 elements becomes 1.01 ± 0.03. For the 8 siderophiles (Re-Au) mean L6/L5 ratios are also at or near unity (Fig. 1), the overall mean being 1.06 ± 0.13 (Table 5). Two Kuttippuram data—for Mo and Co—are somewhat elevated (Table 2): their omission yield a mean L6/L5 ratio of 1.03 ± 0.09 for these 8 siderophiles. The L6/L5 ratios for the 6 moderately volatile elements (Li-Sn) are close to unity and yield an overall mean of 0.96 ± 0.05 (Table 5). As expected, geometric mean L6/L5 ratios for the 11 highly mobile elements, (Ga-Cd) are much more variable than for the other 38 elements even though only mildly shocked (S1-S3) L5 and L6 chondrites are depicted in Figure 1. The overall L6/L5 geometric mean for these 11 elements in 1.23 ± 0.56 (Table 5).

Clearly, mean data for the 38 refractory lithophile, siderophile and moderately volatile elements fail to reveal an obvious compositional difference between mildly shocked L5 and L6 chondrites. While the data for the 11 highly mobile trace elements are less definitive in this regard, at face value they yield a conclusion at odds with conventional wisdom. If thermal metamorphism of common parent material in an open system took place, one would expect L6 chondrites to contain lesser quantities of highly mobile trace elements than L5 and the resulting L6/L5 ratios should be <1.0. Although the L6/L5 ratio is >1.0, one might argue that the standard deviation of ±0.56 could conceal the commonly expected result. Before discussing this possibility further, we will use our multivariate statistical techniques to test for compositional uniqueness.

Figure 2 depicts LDA and LR results using all 49 trace elements to classify the mildly shocked L5 and L6 chondrites. Model-dependent separation is perfect and highly significant statistically, with $p \ll 0.001$. This is not an unexpected result in view of the large number of elements involved. To test our hunch of compositional over-determination, we carried out a "reconnaissance" with 10 randomization-simulations using LR (which Lipschutz and Samuels, 1991, and we consider the more robust) and data for the 49 elements in 9 randomly chosen "L5" chondrites with the remaining 8 "L6" chondrites. In all 10 cases, separation was identical to that in Figure 2, i.e., no misclassifications. Thus, LR can separate the L5 and L6 chondrites based on chemical composition. Although some may accept these model-dependent results, we do not, since perfect separations result when random inputs of so-called "L5" and "L6" chondrites are used with the LDA and LR metrics.

In compositionally over-determined comparisons such as this (Fig. 2), model-independent statistical significance can often be demonstrated if fewer elements are treated, the elements being "shaved" (i.e., omitted) using a meaningful physical or geochemical criterion, not a statistical one (Lipschutz and Samuels, 1991; Wolf and Lipschutz, 1998, and references therein). However, with 49 elements as in Figures 1 and 3, the criterion for omitting one or more is not obvious and could be debated.

We chose, then, to test each pair of L chondrite subsets using each of the four elemental subgroups. Thus, in comparing compositional data for L5 and L6 chondrites, we repeated LR model-dependent, and model-independent randomization-simulations using the LR metric in reconnaissance mode for the following compositional subsets: refractory lithophiles and siderophiles; lithophiles; siderophiles; moderately volatile elements; highly volatile elements.

In each case, we obtained a model-dependent LR result like that illustrated in Figure 2 with no misclassifications. Model-independent randomization-simulations for nearly every group of elements (even omitting a few of the least or most volatile/mobile ones) were not statistically significant. Only one of these even approached significance at $p = 0.1$, the comparison based upon the 6 most volatile of the 8 siderophiles. While suggestive, this model-independent result (and/or the others) is inadequate to reject the null hypotheses of identical composi-

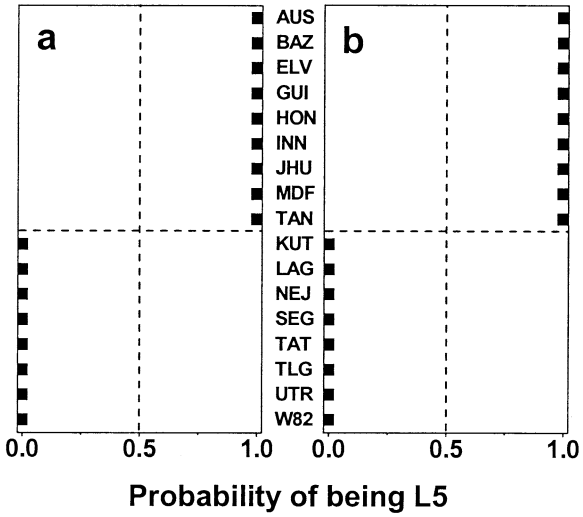

Fig. 2. Very strong, model-dependent evidence for a compositional difference between 9 mildly shocked L5 and 8 mildly shocked L6 chondrites based upon data for 49 trace elements using (a) linear discriminant analysis (LDA) and (b) logistic regression (LR). In each case, no misclassification occurs and the corresponding p-value is $\ll$0.001. However, using randomization-simulation of 10 trials in each case also yielded 0 misclassifications so that on a model-independent basis, the significance of the L5/L6 comparisons are indeterminate (see text).

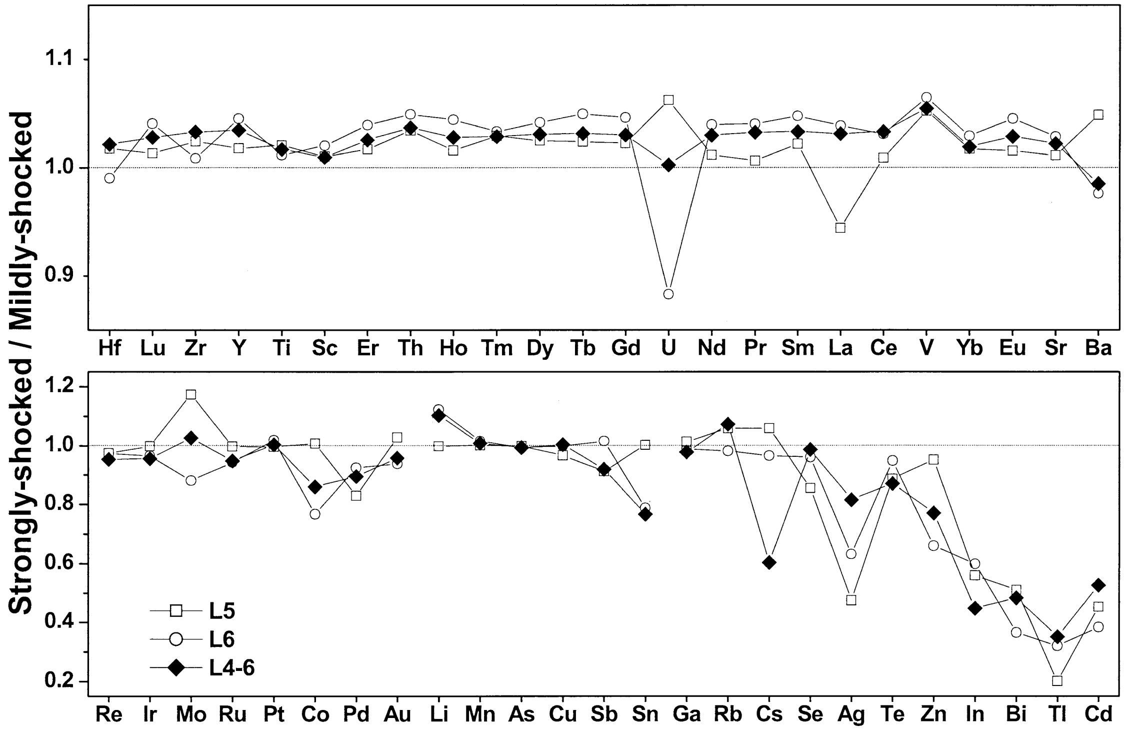

Fig. 3. Strongly shocked L5 (n = 5), L6 (n = 20), and L4-6 (n = 26) chondrite means, respectively, normalized to those of mildly shocked L5 (n = 9), L6 (n = 8), and L4-6 (n = 19) chondrites, respectively, for 24 refractory lithophiles (Hf-Ba), 8 refractory siderophiles (Re-Au), 6 moderately volatile (Li-Sn), and 11 highly volatile and thermally labile (Ga-Cd) elements. Means and associated standard deviations for 24 refractory lithophiles (L5: 1.02 ± 0.02, L6: 1.03 ± 0.04, L4-6: 1.03 ± 0.01) among highly shocked and mildly shocked L5, L6, and L4-6 chondrites hint at small differences. Eight refractory siderophiles (Re-Au), with respective means and standard deviations of 1.00 ± 0.09, 0.93 ± 0.07, and 0.95 ± 0.05, show little evidence for a difference in the L5 suite, but hint at a depletion in the L6 and L4-6 suites. The pattern of the 17 moderately to highly volatile elements seems to decrease with increasing putative volatility (left to right). Multivariate statistical treatments of data for these elements clarify the picture and demonstrate statistical differences.

tions of mildly shocked L5 and L6 chondrites. Thus, no compelling evidence exists for a compositional difference arising during metamorphism of the L chondrite parent(s), i.e., solely as a function of petrographic type. In any event, our data present no significant evidence indicative of more severe compositional alteration (especially mobile element loss) in mildly shocked L6 falls than in analogous L5s. We could suggest at least one ad hoc explanation to account for the face value enrichment observed in the highly labile elements, Ga-Cd, but we see no merit in such speculation.

Whether it was early shock-loading and related heating with subsequent annealing (Rubin et al., 2001; Rubin, 2002, 2003) or radiogenic heating (cf. McSween et al., 1988) that were responsible for the observed thermal metamorphism of the L chondrite parent(s), our data are consistent with the heating episode(s) having occurred in a closed system with respect to both refractory and volatile trace elements. We will further examine the proposal that shock-induced heating might have been a heat-source for metamorphism when we discuss shock-loading.

4.2. Compositional Variations with Shock-Loading

To investigate the effect of shock-loading on L chondrite compositions, we will consider 2 population subsets: 19 mildly shocked (S1-S3) and 26 strongly shocked (S4-S6) L4-6 chondrites; and 8 mildly and 20 strongly shocked L6 samples only. The S3 and S4 stages constitute a logical separation because the estimated minimum residual temperature increase due to shock-loading is substantial, 100°C versus 300°C between these shock stages (Stöffler et al., 1991). It also separates our L4-6 samples into roughly equal subsets. We exclude three samples from consideration: Rio Negro, Atarra, and Louisville dark. The first two are compositionally problematic (see above). The third, Louisville dark, was a large L chondrite-dark inclusion contained within the larger Louisville sample (Louisville light). However, we have no shock stage classification for this unique fragment.

4.2.1. *Elemental Trend Comparisons*

In Figure 3, we depict mean concentrations for lithophiles, siderophiles, moderately volatile and highly mobile elements as strongly shocked/mildly shocked ratios for L5, L6, and L4-6 chondrites. We will first consider the effects of shock loading on the L4-6 suite as a whole. While the most striking effects involve the highly mobile elements, Ga-Cd, other groups of elements show important systematic trends. The 24 refractory lithophiles, Hf-Ba, seem systematically enriched at 1.03 ± 0.01 (Fig. 3, Table 5). This is not surprising since these elements are

Table 6. Mean contents and related 1σ standard deviations of major elements in the two L4-6 chondrite suites of falls whose trace element data are reported in Table 1.

Suite[a]	SiO_2	MgO	FeO	Fe_{metal}	Fe_{total}	FeS
Mildly shocked (n = 12)	39.5 ± 0.5	24.5 ± 0.4	14.3 ± 0.6	7.2 ± 1.2	22.5 ± 0.3	6.1 ± 0.7
Strongly shocked (n = 25)	39.8 ± 0.6	24.9 ± 0.4	14.5 ± 1.2	7.0 ± 1.0	21.9 ± 0.3	5.6 ± 0.9

[a] Data from Jarosewich (1990). Baszkówka, Innisfree, Saratov, Tennasilm, Monte das Fortes, Tané, and Farmington not included (see section 4.2.1).

contained in residues "enriched" because of loss of other elements from strongly shock-heated material in an open system. Eight siderophiles, Re-Au, lie somewhat below the line at unity (Fig. 3), their mean being 0.95 ± 0.05 (Table 5). We interpret their depletion as reflecting loss from strongly shock-heated material, probably by open-system extraction in Fe,Ni-FeS eutectic partial melt material, that forms at ~980°C on a scale larger than that of our samples.

To examine this idea further, we list in Table 6 mean major element contents determined using wet-chemistry by Jarosewich and coworkers for many of the same mildly and strongly shocked L4-6 chondrite falls of this study. Although occasional major element data collected by others than Jarosewich are available for Baszkówka, Innisfree, Saratov, Tennasilm, Monte das Fortes, Tané, and Farmington, we do not include them here to avoid analyst bias. While the mean compositional differences between the two suites are exceeded by the analytical uncertainties (Table 6), they are consistent with the trace element data (Table 5). At face value, the major element data show ~2% iron and ~7% sulfur deficits in the strongly shocked suite relative to the mildly shocked one. Assuming that the iron was lost as Fe,Ni-FeS eutectic, the corresponding Fe and S deficits would be ~2.6%, in good agreement with the refractory lithophile enrichment level of 0.03 ± 0.01. Any additional sulfur loss could reflect vaporization with highly mobile elements, signaled by radiogenic noble gas loss and the depletion of the 11 trace elements Ga-Cd (Fig. 3) to a mean of 0.68 ± 0.37 (Table 5) in L4-6 chondrites. The trend for the 6 moderately volatile elements, Li-Sn (Fig. 3), is consistent with this picture. Its mean ratio, 0.97 ± 0.11 (Table 5), is close to unity, with smaller open-system losses of some elements being essentially balanced by enrichment of refractories.

To examine whether effects of shock-loading in L5 and L6 chondrites differ, we may consider the strongly shocked/mildly shocked ratios for each petrographic type separately (Fig. 3). In general, the trends for L5 and L6 do not differ markedly from those of L4-6 (Fig. 3). (The U, La, Ba and Mo anomalies in the L5 and L6 data obviously reflect occasional aberrances in individual samples; Table 2.) For example, mean ratios for the 24 refractory lithophiles in L5, L6 and L4-6 subsets are 1.02 ± 0.02, 1.03 ± 0.04 and 1.03 ± 0.01, respectively, and 0.66 ± 0.52, 0.66 ± 0.44 and 0.68 ± 0.37, respectively, for 11 highly mobile trace elements (Fig. 3, Table 5). Means for siderophiles and moderately volatile elements are also similar (Fig. 3, Table 5). If establishment of petrographic type for L chondrites were linked to and/or initiated by early shock-related heating events (Rubin, 2002, 2003), we might expect labile element compositional differences to be more striking in L6 than in L5 falls. However, our data do not bear this out (Fig. 3; Table 5). If any preshock, compositional differences existed involving volatile and refractory trace element contents, severe open-system heating caused by the shock(s) could well have obscured this, particularly for volatiles.

4.2.2. Statistical Comparisons

Shock-induced compositional alteration of L chondrites proves of greater significance than that associated with metamorphism in L parent(s), and we will use the descriptive terms very strong evidence, strong evidence and moderate evidence to imply $p \leq 0.001$, $0.001 < p \leq 0.01$ and $0.01 < p \leq 0.1$, respectively, in discussing statistical results. A *p*-value is the likelihood of incorrectly rejecting the null hypothesis (mildly shocked and strongly shocked L4-6 chondrites are compositionally identical) if it is, in fact, true. In other words, the smaller the *p*-value, the more significant the compositional difference between the two groups. When using data for 49 trace elements, LDA and LR classify 19 mildly shocked and 26 strongly shocked L4-6 chondrites and 8 mildly shocked and 20 strongly shocked L6 chondrite falls. On a model-dependent basis, each of these provides very strong evidence ($p < 0.001$) for a compositional difference between mildly and strongly shocked subsets. As promising as these results seem, they do not prove statistically significant on a model-independent basis. The classifications are so over-determined that for 100 randomization-simulations each, the LDA or LR metrics yield zero misclassifications in at least 60%, usually 100%, of the runs. However, unlike the case depicted in Figure 2, where we considered a possible compositional dependence with petrographic type in mildly shocked L5 and L6 falls, we can demonstrate a significant compositional dependence with shock-loading on a model-independent basis.

For their full L4-6 chondrite suite (9 mildly and 24 strongly shocked), Lipschutz and Samuels (1991) found, on a model-independent basis using the LR metric, a moderately strong difference ($p = 0.044$) using 11 elements, mainly highly mobile ones (Table 7). Using just the 4 least mobile of these, the difference became stronger ($p = 0.009$): however, using the LDA metric, no compositional dependence could be demonstrated on a model-independent basis, no matter how few highly mobile elements Lipschutz and Samuels (1991) used (Table 7).

For the same 11 elements used by Lipschutz and Samuels (1991), and our larger L4-6 chondrite suite (19 mildly and 26 strongly shocked falls), multivariate test results proved to be more convincing. We found 8 and 4 misclassifications using LDA and LR, respectively, with the latter being strongly significant on a model-dependent basis (Table 7). For 1000 randomization-simulations each, using the LDA and LR metrics, we found 51 and 7, respectively, having no more than the corresponding 8 and 4 misclassifications (Table 7). Hence, on

Table 7. Significant compositional differences between mildly shocked and strongly shocked L chondrite falls.

	Lipschutz and Samuels (1991)					
Suites compared	Multivariate technique	Test population	No. elements	No. misclass	p value: Model dependent	p value: Model independent
9 mildly, 24 strongly shocked L4-6	LDA	Co, Au, Ga, Rb, Cs, Te, Bi, Ag, In, Tl, Zn	11	2	0.052	—
	LR	Co, Au, Ga, Rb, Cs, Te, Bi, Ag, In, Tl, Zn	11	0	<0.001	0.044
	LR	Co, Au, Rb, Zn	4	6	0.021	0.009
	This Work					
Suites compared	Multivariate technique	Test population	No. elements	No. misclass	p value: Model dependent	p value: Model independent
19 mildly, 26 strongly shocked L4-6	LDA	Hf-Cd (All)	49	0	0.048	—
	LR	Hf-Cd (All)	49	0	<0.001	—
	LDA	Co, Au, Ga, Rb, Cs, Te, Bi, Ag, In, Tl, Zn	11	8	0.111	0.051
	LR	Co, Au, Ga, Rb, Cs, Te, Bi, Ag, In, Tl, Zn	11	4	0.003	0.007
	LR	Co, Au, Rb, Zn	4	12	0.0005	0.051
	LDA	Ga, Rb, Cs, Se, Ag, Te, Zn, In, Bi, Tl, Cd	11	7	0.076	0.017
	LR	Ga, Rb, Cs, Se, Ag, Te, Zn, In, Bi, Tl, Cd	11	7	0.006	0.059
	LDA	Hf, Zr, Y, Ti, Sc, Th, U, V, Sr, Ba	10	8	0.016	0.040
	LR	Hf, Zr, Y, Ti, Sc, Th, U, V, Sr, Ba	10	7	0.003	0.023
	LDA	Re, Ir, Mo, Ru, Pt, Co, Pd, Au	8	10	0.022	0.072
	LR	Re, Ir, Mo, Ru, Pt, Co, Pd, Au	8	8	0.004	0.014
8 mildly, 20 strongly shocked L6	LDA	Hf-Cd (All)	49	0	<0.001	—
	LR	Hf-Cd (All)	49	0	<0.001	—
	LR	Pt, Co, Pd, Au	4	3	<0.001	0.009

a model-independent basis, the compositional distinction between mildly and strongly shocked L4-6 falls is moderately strong using the LDA metric and stronger using the LR metric (Table 7). Repetition of the LR comparison (cf. Lipschutz and Samuels, 1991) using only Co, Au, Rb, Zn with our larger suite of L4-6 chondrites yielded a highly significant model-dependent *p*-value, and a moderately significant model-independent result (Table 7). Because of the greater number of samples, particularly of mildly shocked (S1-S3) falls, our results should be somewhat more definitive than those of Lipschutz and Samuels (1991) for the same elements.

In considering our approach to this study, we must be self-consistent and since the element suite studied by Lipschutz and Samuels (1991) included 2 siderophiles, Co and Au, we reran the multivariate tests replacing these with Se and Cd. The model-dependent LDA and LR results (Figs. 4a,b) for our suite of highly mobile trace elements do not differ markedly from those of Lipschutz and Samuels (1991). Our significance levels are moderate-to-strong (Table 7) and 7 misclassifications occurred for each (Figs. 4a,b). On a model-independent basis, we found 7 or fewer misclassifications in 17 and 59 of the 1000 randomization-simulations using the LDA and LR metrics, respectively (Figs. 4c,d). Hence, moderate model-independent evidence exists for a compositional difference between mildly and strongly shocked L4-6 chondrites using *highly mobile* elements alone (Table 7).

Model-dependent LDA and LR of data for the 24 refractory lithophiles, Hf-Ba, reveals perfect separation of mildly and strongly shocked L4-6 falls with no misclassifications, like Figure 2. The separation is over-determined and neither is significant using all 24 lithophiles. Since the 14 REE behave as one and Sc and Y act as reasonable proxies, we omitted all 14 REE: model-dependent LDA and LR using the remaining 10 lithophiles are depicted in Figures 5a and b. Model-dependent significance levels are 0.016 and 0.003 with 8 and 7 misclassifications, respectively (Table 7). For 1000 randomization-simulations each, LDA and LR metrics produce 40 and 23 runs with as many as 8 and 7 misclassifications, respectively (Table 7). We may conclude therefore that, as is the case with highly volatile elements, *refractory lithophiles* provide moderate evidence for a shock-associated compositional difference of L4-6 falls (Table 7; cf. Table 6).

For the 8 siderophiles (Re, Ir, Mo, Ru, Pt, Cs, Pd, Au), model-dependent LDA and LR (Figs. 6a,b) indicate moderate to strong evidence ($p = 0.022$ and $p = 0.004$, respectively) for a compositional difference between 19 mildly and 26 strongly shocked L4-6 chondrites. The 19 and 8 misclassifications, respectively, of Figures 6a and 6b, are equaled or bettered in 72 and 14 runs, respectively, of 1000 randomization-simulations using the corresponding LDA (Fig. 6c) and LR (Fig. 6d) metric. Thus, moderate evidence ($p = 0.072$ and $p = 0.014$) exists for a compositional distinction related to shock-loading involving *siderophiles*.

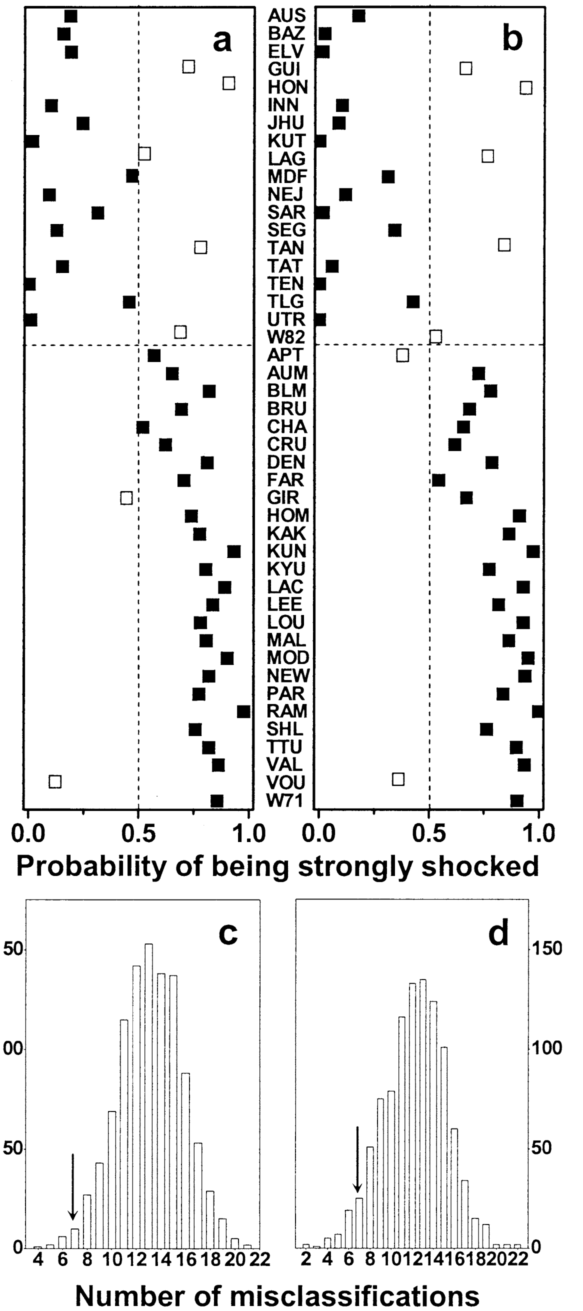

Fig. 4. Moderate evidence for a significant compositional difference between 19 mildly shocked and 26 strongly shocked L4-6 chondrites based on data for 11 thermally labile trace elements (Ga, Rb, Cs, Se, Ag, Te, Zn, In, Bi, Tl, Cd) using: (a) LDA; and (b) LR. Using LDA and LR, 7 misclassifications result in each case, indicating model-dependent *p*-values of 0.076 and 0.006 respectively. Using 1000 randomization-simulation trials in the LDA case (c) results in 17 runs yielding 7 or fewer misclassifications: in the LR case (d) 59 runs yield 7 or fewer misclassifications (indicated by arrows). Thus, on a model-independent basis, classification of these chondrites is moderately significant (*p*-value of 0.017) with LDA and strongly significant (*p*-value of 0.059) with LR (see text).

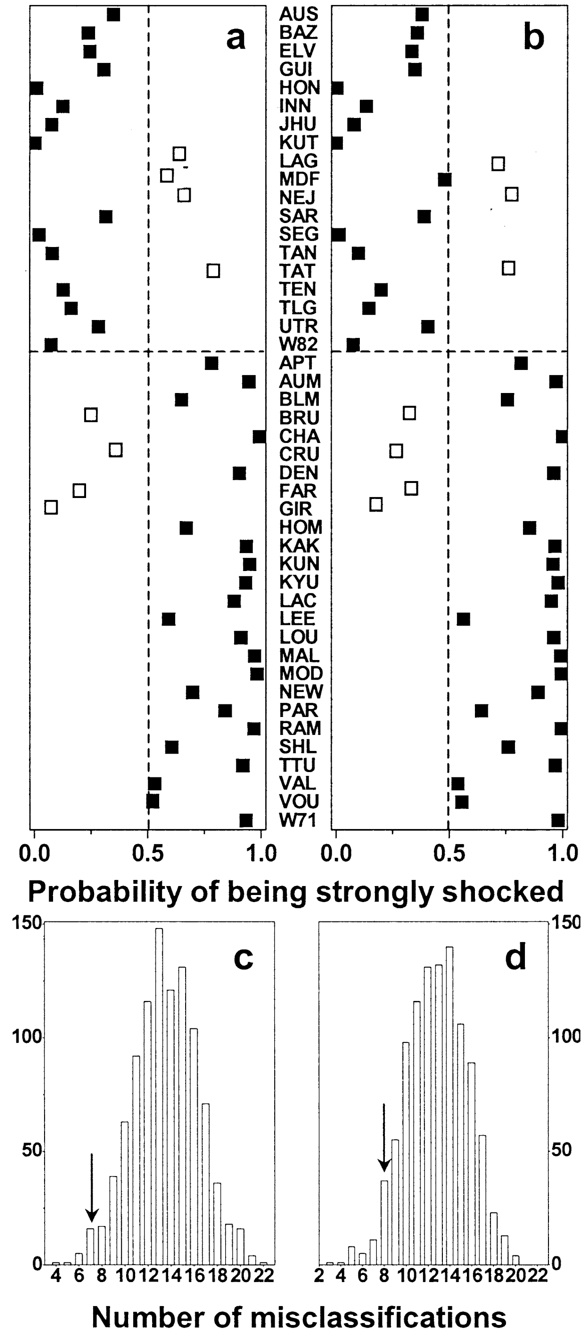

Fig. 5. Moderate evidence for a compositional difference between 19 mildly shocked and 26 strongly shocked L4-6 chondrites based on data for 10 non-REE, refractory, lithophile elements (Hf, Zr, Y, Ti, Sc, Th, U, V, Sr, Ba) using: (a) LDA and (b) LR. Using LDA and LR, 8 and 7 misclassifications result respectively, with corresponding model-dependent *p*-values being 0.016 and 0.003. Using 1000 randomization-simulation trials in the LDA case (c) results in 40 runs with ≤8 misclassifications, and in the LR case (d) 23 runs with ≤7 misclassifications (indicated by arrows). Thus, using 10 on a model-independent basis, classification of these chondrites is moderately significant with *p*-values of 0.040 and 0.023 respectively (see text).

As discussed earlier, very strong model-dependent evidence exists for a compositional difference involving all 49 elements of our suite (Hf-Cd) for 8 mildly and 20 strongly shocked L6 chondrites. For these L6 subsuites, reconnaissance using the LR metric provided moderate, model-independent evidence for compositional distinction from the 4

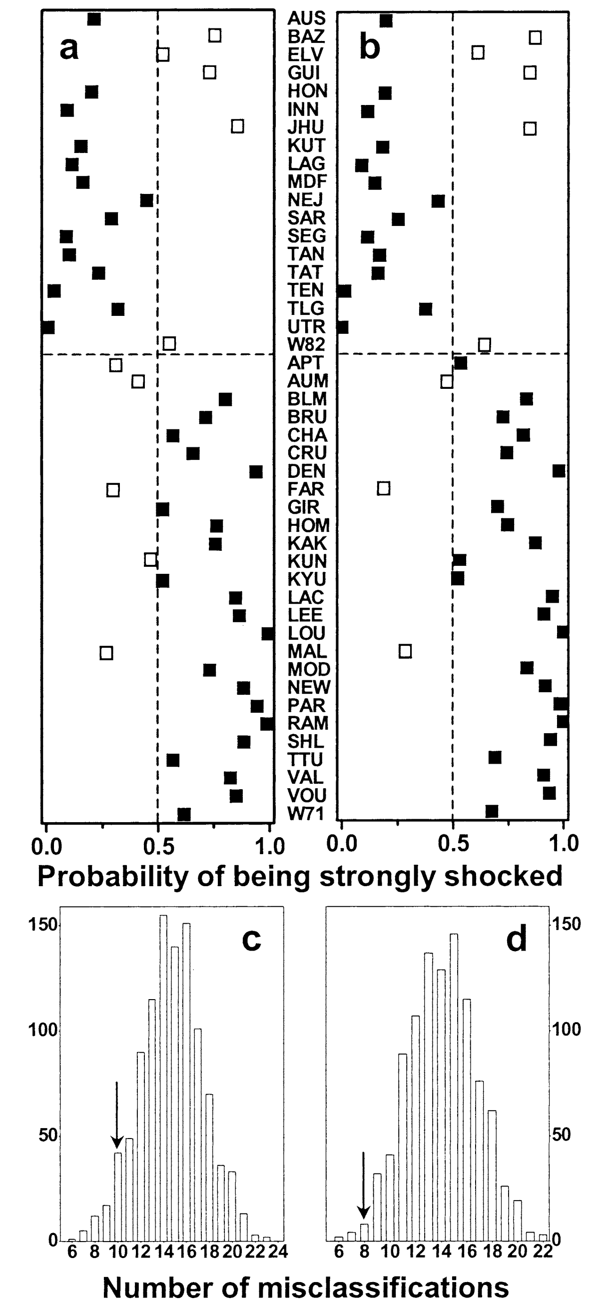

Fig. 6. Moderate to strong evidence for a significant compositional difference involving 8 siderophiles (Re-Au) between 19 mildly and 26 strongly shocked L4-6 chondrites. LDA (a) and LR (b) yield 10 and 8 misclassifications, respectively, and moderate ($p = 0.022$) and strong ($p = 0.004$) evidence for a model-dependent compositional difference between these sample suites. A thousand randomization-simulation runs for each of these suites using LDA (c) and LR (d) metrics yield moderate evidence for a model-independent compositional difference (p-values of 0.072 and 0.014, respectively) between these L4-6 chondrite groups (see text).

most volatile siderophiles, Pt-Au (Table 7). Other results were indeterminate.

4.3. General Evolutionary Implications

1. In comparing mildly shocked L5 and L6 chondrites compositionally, two salient points emerge. Using data for all 49 trace elements, model-dependent LDA and LR produce very strong evidence disproving the null hypothesis that mildly shocked L5 and L6 chondrites are compositionally identical (Fig. 2). However, model-independent randomization-simulations of all or part of the data fail to disprove this null hypothesis at an acceptable statistical level (Section 4.1). The abundance patterns for the 49 trace elements in these L5 and L6 are essentially identical (Fig. 1). If there is a difference involving highly volatile elements, these differences have been obscured by any later open-system shock events. 2. Compositionally, mildly shocked L4-6 chondrites differ significantly from strongly shocked ones. Model-dependent LDA and LR treatment involving all 49 trace elements disprove the null hypothesis of compositionally identical mildly and strongly shocked L4-6 chondrites (Fig. 5). Subsets of these elements (refractory lithophiles, siderophiles, moderately volatile and highly mobile elements) disprove this null hypothesis equally strongly on a model-dependent basis. However, to us, it is more important that 3 subsets of these elements disprove this null hypothesis on a model-independent basis. Ten refractory lithophiles, 8 siderophiles and 11 highly volatile elements treated using the LDA and LR metrics (Figs. 4–6) show this at moderate to strong significance levels (Table 7). The same conclusion can even be reached for mildly and strongly shocked L6 chondrites alone, if the 4 most volatile siderophiles are treated by randomization-simulation using the LR metric (Table 7).

3. Compositional patterns for mildly and strongly shocked L4-6 chondrites (or for L5 and L6 treated separately) indicate that shock-generated, high temperatures (above ~980°C) and extended cooling were primarily responsible for the open-system fractionations. Highly mobile elements (Ga-Cd) were vaporized and lost (cf. Huston and Lipschutz, 1984, and references therein) and siderophiles (Ru-Au) were extracted, presumably into Fe,Ni-FeS eutectic, and transported away from highly shock-loaded regions (Fig. 3). Because of these losses, highly refractory lithophiles were somewhat enriched in these labile- and siderophile/chalcophile/mobile element–depleted regions (cf. Table 6). It is worth noting in this connection that siderophiles are significantly depleted in the lithic (impact melt) phases of the L6 (S6) chondrite, Chico (Norman and Mittlefehldt, 2002, and references therein). Additionally, Horan et al. (2003) report that several chondrites exhibit "high and low domains" of refractory siderophiles because of shock (re)heating.

5. CONCLUSIONS

The multivariate statistical techniques of linear discriminant analysis (LDA) and logistic regression (LR) can prove useful when treating compositional data for quite strongly fractionated sample populations (Wolf et al., 1997, and references therein). However, model-dependent LDA and LR and their model-independent adaptation (randomization-simulation) are also productive in studying populations differing more subtly, such as our suites of L chondrites.

Our ICPMS and RNAA data for 49 trace elements in 45 L4-6 chondrites reveal no large compositional difference between mildly shocked (S1-S3) L5 and L6 chondrites. Using LDA and LR, these 8 L5 and 9 L6 chondrites are distinguishable at very strong, model-dependent statistical levels. However, using model-independent randomization-simulations, this separation cannot be verified. Thus, no evidence exists that mildly shocked L5 chondrites are volatile-rich compared with L6 samples.

However, mildly shocked (S1-S3) L4-6 chondrites can be compositionally distinguished from strongly shocked (S4-S6) L4-6 samples. Using model-dependent LDA and LR to treat data for 49 elements, mildly and strongly shocked L4-6 (or L6) chondrites are distinguishable with very high confidence. Model-independent results using all 49 trace elements prove indeterminate. Nevertheless, when the elements are grouped as 24 refractory lithophiles, 8 siderophiles, 6 moderately volatile and 11 highly mobile ones, moderately strong, model-independent differences can be demonstrated for 3 of these (all but the moderately volatile elements). The ultimate cause for these observed postaccretionary compositional alterations in highly shocked L4-6 chondrite falls is impact shock-heating and the slow cooling of collisional debris from high residual temperatures. Two major effects are the result of this heating. First, localized (<1 m) parent body metal/silicate partitioning due to temperature at or near the Fe,Ni-FeS eutectic (~980°C) led to a slight net loss of siderophiles and slight net gain of lithophiles in strongly shocked material. Second, there was volatilization and significant loss of mobile trace elements (and noble gases, particularly of radiogenic origin).

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