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Trace Element Contents of Selected Antarctic Meteorites -I.

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Dedicated to Professor H. Hintenberger

on the occasion of his 70th birthday.

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Abstract - We report data for volatile/mobile Ag, As, Au, Bi, Cd, Co, Cs, Cu, Ga, In, Rb, Sb, Se, Te, Tl and Zn in exterior and/or interior samples of four Antarctic meteorites: 77005 (unique achondrite); 77257 (ureilite); 77278 (L3); 77299 (H3). Exterior samples reflect contamination and/or leaching by weathering but trace element (ppm-ppt) contents in interior samples seem reasonable for representatives of these rare meteoritic types. The 77005 achondrite seems related to shergottites; other samples extend compositional ranges previously known for their types. With suitable precautions, Antarctic meteorite finds yield trace element data as reliable as those obtained from previously - known falls.

INTRODUCTION

Among the large numbers of meteorites discovered recently in the Yamato Mts. and Allan Hills regions of Antarctica have been several representatives of rare or previously-unknown classes. Doubtless, such discoveries will continue, increasing the kinds of extraterrestrial material available for study. However, Antarctic meteorites can have substantial terrestrial ages; 1.5 x 10^6 years was determined in one case by Fireman et al. [1](cf. Evans and Rancitelli [2], Melcher [3]). Many of these are badly-weathered and have clearly been compromised for some purposes, particularly trace element studies. On the other hand, some meteorites-denoted Type A by the Meteorite Working Group (MWG) - show little or no signs of weathering and, if at all fractured, are only slightly so. Portions of such specimens might well be useful for trace element studies.

We felt it desirable to determine trace element contents in several Type A meteorites of rare or previously unknown classes and to evaluate weathering effects by analyzing exterior, mid and/or interior portions of some of these. Since, a priori, weathering might either be reflected in trace element loss through leaching or enrichment by contamination, we chose to study both volatile-rich (L3) and volatile-poor (ureilite) meteorites, thus providing material suitable for enhancing both effects. We chose to determine 16 elements -Ag, As, Au, Bi, Cd, Co, Cs, Cu, Ga, In, Rb, Sb, Se, Te, Tl, Zn - because these represent all geochemical classes but atmophile elements and many yield important information on genetic fractionation processes (Anders [4];cf. Binz et al. [5], Matza and Lipschutz [6] and references cited in these papers). In addition, some of these elements are extraordinarily resistant to weathering while others seem strongly affected (e.g. Binz et al. [5,7]).

EXPERIMENTAL

All specimens studied were obtained from the NASA Johnson Space Center portions and were taken from the following approximate depths (i.e. to the nearest surface) in the specimens: 77005, 23 (unique achondrite) - 1 cm.; 77257, 17 (ureilite) - 0 cm., 29 - 1 cm., 32 - 2 cm.; 77278, 18 (L3) - 0 cm., 20 - 4 cm.; 77299, 22 (H3) - 2 cm.. We decided to analyze 77005, 23 and 77278, 20 in duplicate; each sample analyzed was ∿ 0.2 g. For reference, dimensions of the whole rocks reported by the MWG are: 77005 - 9.5 x 7.5 x 5.25 cm.; 77257 - 16 x 11 x 9.5 cm.; 77278 - 8.0 x 5.5 x 4.5 cm.; 77299 - 9.5 x 5.5 x 3.5 cm.

Samples were prepared for irradiation as in Ikramuddin et al. [8]. All irradiations were 4 - days' long and were performed at the University of Missouri research reactor; fluxes were ∿ 1.2×10^{14} neutrons $/cm^2/sec$. While the neutron flux was less thermalized than that in the Argonne CP-5 reactor we used previously, results from Allende standard reference meteorite powder irradiated in both reactors by Ngo [9] were quite comparable and indicated no self-shielding effects for the elements considered here. Chemical and counting procedures, summarized in part by Ngo [9], for most elements were generally modifications of those described by Binz et al. [5], Ikramuddin et al. [8] and Bart et al. [10]. Additional elements - As, Cu, Rb, Sb - were interposed in the analytical scheme with As, Rb and Sb being precipitated as sulfides in acid medium from the supernate after precipitation of basic sulfides from the dissolved Na_2O_2-NaOH fusion cake. Copper was precipitated as sulfide from the Co, In effluent from the anion exchange column. After additional purification steps, these elements were precipitated individually - As and Sb as metals, Cu as CuSCN and Rb as the tetraphenylborate. Average chemical yields were Ag (57%), As (50%), Au (35%), Bi (27%), Cd (68%), Co (58%), Cs (30%), Cu (34%), Ga (20%), In (35%), Rb (38%), Sb (22%), Se (34%), Te (38%), Tl (46%), Zn (55%). Monitor yields were substantially higher because of abbreviated cleanup procedures. Counting and data reduction procedures were essentially those used previously. Copper deserves special note since we counted 511 keV annihilation radiation; we assured radiochemical purity by following 12.7 hour ^{64}Cu decay for five half-lives and analyzing the data by the CLSQ program of Cumming [11]. For some purposes, it is necessary to convert concentration data to atomic abundances relative to Si; we used Si values for 77005 and 77257 provided by Ehmann and Young [12] and 18.7 and 17.1% Si for 77278 and 77299, respectively, as reviewed by Moore [13].

RESULTS AND DISCUSSION

Included with our results in Table 1 are the larger of uncertainties calculated in two ways. About half of these are uncertainty estimates derived from previous analyses in our laboratory of Allende standard meteorite reference material by Ngo [9]; Bart et al. [10] and Ikramuddin and Lipschutz [14]; they are probably conservatively high because of minor processing changes in these studies. In the other half, duplicate analyses of interior parts of 77005 and 77278 yield sample variances greater than uncertainties estimated from Allende data. Thus, uncertainties listed are calculated from the dispersion of Antarctic meteorite data; these are suggestive of heterogeneity effects on the 0.2 g - scale.

For many elements, results for 77257 and 77278 indicate significant differences between interiors and other parts of each meteorite; we attribute these to weathering. Both in the ureilite and L3 chondrite, exterior parts are enriched in Cs and Rb; seemingly these elements are slightly enriched at the 1 cm. depth in the former (Table 1). Other elements show different trends. Silver, Cd and Sb are enriched in the surface of the ureilite (and, for Sb, at 1 cm.depth) but not in 77278; in fact, Sb (and possibly Ag) - like Bi, In, Te and Tl - are depleted in the surface of this L3 chondrite. In 77257, Se and Te may be marginally depleted in the surface but In certainly is not. Other elements - As, Au, Co, Cu, Ga and Zn - seem unaffected by weathering in either meteorite. Two data - Co in 77257, 29 and Se in 77278 - seem unusually variable, probably reflecting sample heterogeneity.

We attribute surface enrichments of Cs and Rb in 77257 and 77278 as due to deposition of wind-borne oceanic aerosol. Other elemental enhancements on 77257 must reflect another contamination source since these elements are depleted, presumably by leaching, or are unaffected in 77278. Carbon loss in a C3 and two C2 chondrites (respectively, Yamato 693 and 74662 and ALHA 77306) has also been attributed to leaching by Gibson et al. [15]. Cronin et al. [16] report that amino acid compositions in ALHA 77306 are similar to those in Murchison indicating the absence of contamination but concentrations are factors of 10-40 times lower than in Murchison possibly, but necessarily, by leaching loss. Of the six elements affected by weathering of 77257, Binz et al. [17] found that Cd, Cs and Se are enriched (with Tl) in ureilite finds. Binz et al. [17] did not determine Rb or Sb and Ag was not unusual. Of course, weathering effects could well be different in Antarctica and Western Australia, the source of the ureilite finds studied by Binz et al. [17]. The terrestrial age limit (by thermoluminescence) for 77278 is $\geq 8.8 \times 10^4$ y [3]. Such limits have been determined for only one other meteorite we studied, 77299, for which $\geq 3.5 \times 10^4$ y was reported by thermoluminescence [3] and $< 60 \times 10^4$ y by the better-established ^{26}Al method [2].

Since clear differences for many trace elements exist between exterior and interior portions of 77257 and 77278, it is important to establish whether elemental concentrations in the interiors of Antarctic meteorites are indigenous. Several circumstantial lines of evidence indicate that this is so.

In 77005, all trace elements correlate extremely well with values for terrestrial ultramafic rocks or shergottites, achondrites seemingly related mineralogically to this unique meteorite (cf. McSween et al. [18] for a detailed discussion). It is unlikely that these agreements would be simulated or unaffected by weathering.

Depletion factors or the ratio of an element's atomic abundance in a particular sort of meteorite relative to that in Cl chondrites, for 77257, 32 (derived from data in Table 1) are illustrated in Fig. 1. Also shown are depletion factors for other ureilite finds and falls [17] and for equilibrated ordinary chondrites - which, putatively, are a qualitative measure of elemental nebular volatility [4,5]. Trends in Fig. 1 and in the outer part(s) of ALHA 77257 indicate that the principal weathering effect in ureilites is contamination. If interior parts of 77257 are anything but pristine the contamination process was most peculiar. All sub-samples of this ureilite contain equal concentrations of Cs, Ga and Zn, lying within the corresponding ranges for ureilite falls (Fig. 1).

Data for the other 8 elements in ALHA 77257, 32 are more-or-less uniformly lower than the bottom of the range for ureilite falls. Thus, any contamination would have to have been rather carefully metered - a very unlikely possibility. We believe it far more likely that the composition of 77257, 32 reflects genetic processes (cf. Binz et al. [17]) and that the trace element compositional ranges for ureilite falls must be expanded to include these Antarctic specimens.

Most elements in ALHA 77278, 20 and 77299, 22 (e.g. interior samples) yield depletion factors lying within corresponding ranges for L3 and H3 chondrites, respectively. For 77299, Ag lies below the H3 range and As, Cd, Cs, Cu, Rb, Sb and Te above it; of these, only As and Sb have been analyzed in more than four H3 chondrites (cf. Binz et al. [5]). For 77278, Ag and, marginally, Co and Se lie below the L3 chondrite range while Te, Tl and In lie above it; Ag (and Cs and Rb) are not well-determined in H3 chondrites [5]. Rb/Cs weight ratios for 77278 and 77299 are 8 and 12 respectively, i.e. very reasonable for type 3 and 4 ordinary chondrites and well below ratios > 100 typical of types 5 and 6 [19]. However, contamination levels in the surfaces of 77257 and 77278 yield similar ratios - 14 and 5, respectively - so that agreements may be ambiguous. In unequilibrated ordinary chondrites In and Tl correlate with the disequilibrium parameter for ferromagnesian silicates; Bi is also correlated save in the most unequilibrated case where it is anomalously low [5]. For 77278, In and Tl lie above the known range for L3 chondrites while Bi is well within it but toward the high end (Fig. 2). Indeed, In in 77278 exceeds Cl levels; no other known ordinary chondrite is so enriched (Fig. 2). ALHA 77278 should have a very high disequilibrium parameter and be among the most unequilibrated of L3 chondrites. This possibility is being examined now and, if verified, should provide additional support for the indigenous nature of 77278.

CONCLUSIONS

This study of four Type A Antarctic meteorites demonstrates that weathering effects - like beauty - are only skin-deep and are manifested in trace element loss by leaching and/or enrichment (especially of alkalis) by contamination. The available evidence suggests that interior parts of these cm-sized meteorites (which may have terrestrial ages of 10^4 - 10^5 years) are pristine to the extent that the most weather - sensitive elements were unaffected during exposure in Antarctica. Reliable trace element data - even at the fractional ppb level - can be obtained from such specimens.

While this study of representatives from rare meteorite types - ureilite, L3 and H3 chondrites - does not overturn genetic models for their origin, it strongly suggests that the chemical variability of each of these types is greater than hitherto thought. This variability must be incorporated in existing and future models. Elsewhere we discussed the relationship of the unique achondrite 77005 to the rare shergottite class. We may expect that in the huge Antarctic collection, many additional surprises await and it is gratifying that trace element chemists can do their part in deciphering the histories of such important specimens.

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Table 1. Trace element contents of Antarctic meteorites.

Meteorite	Type	Ag (ppb)	As (ppb)	Au (ppb)	Bi (ppb)	Cd (ppb)	Co (ppm)	Cs (ppb)	Cu (ppm)	Ga (ppm)	In (ppb)	Rb (ppb)	Sb (ppb)	Se (ppm)	Te (ppb)	Tl (ppb)	Zn (ppm)
ALHA 77005	Achondrite																
,23	interior	3.89	1.33	0.292	-	5.87	65.3	38.0	5.41	6.01	10.[illegible]	502	0.87	0.120	0.43	1.94	47.9
		4.85	1.41	0.284	0.32	5.97	69.0	38.6	5.52	6.13	12.0	750	0.50	0.177	0.46	1.46	50.8
	mean*	4.37	1.37	0.288	≤0.72	5.92	67.2	38.3	5.46	6.07	11.1	626	0.68	0.149	0.45	1.70	49.4
		±0.68	±0.21	±0.007		±0.58	± 2.6	± 1.4	±0.10	±0.54	± 1.3	±175	±0.26	±0.040	±0.05	±0.34	± 2.0
ALHA 77257	Ureilite																
,17	exterior	2.14	236	20.1	≤0.9	20.8	109	0.78	3.20	1.63	0.35	8.28	10.0	0.228	18.0	≤0.04	269
,29	mid-portion	1.85	206	20.6	≤0.9	4.5	83.4	0.34	3.07	1.72	0.32	1.95	7.99	0.222	22.6	≤0.04	282
,32	interior	1.92	273	20.4	≤0.9	4.9	109	0.29	3.23	1.8	0.36	1.30	4.96	0.257	22.4	≤0.04	273
ALHA 77278	L3																
,18	exterior	33.5	1280	124	32.7	104	467	648	78.0	5.48	84.4	4560	28.9	7.82	521	89.4	57.6
,20	interior	40.5	1220	127	-	106	425	402	87.4	5.86	16[illegible]	3020	66.6	2.22	862	144	55.5
		38.9	1150	-	39.6	94.8	422	407	75.0	5.61	215	3860	46.7	10.7	881	112	61.2
	mean*	39.7	1190	127	39.8	100	424	405	81.2	5.74	190	3440	56.8	6.5	872	128	58.4
		± 1.6	± 180	± 3	± 0.6	± 8	± 15	± 15	± 8.8	±0.51	± 36	± 590	± 8.6	±6.0	±100	±11	± 4.0
ALHA 77299	H3																
,22	interior	38.2	2340	[illegible]	45.9	91.2	716	319	110	7.09	49.3	3820	157	-	487	21.8	56.2

Notes to Table 1.

*Mean values listed are for interior samples only. Uncertainties are 1 σ values calculated from the dispersion of replicate analyses of Allende reference standard [9, 10, 14] or chips of the particular Antarctic meteorite. Uncertainties listed are the larger of the two values: italics indicate cases where values for Allende exceed those for the Antarctic meteorite itself and uncertainties in normal type denote the opposite.

Table 2. Trace element contents in external parts of ureilite and L3 chondrite relative to those of interior.

Interior-normalized contents

	77257*		77278*
	exterior	mid-section	exterior
Ag	1.11	0.96	0.84
As	0.86	0.75	1.08
Au	0.98	1.01	0.98
Bi	—	—	0.82
Cd	4.22	0.91	1.04
Co	1.00	0.77	1.10
Cs	2.69	1.17	1.60
Cu	0.99	0.95	0.96
Ga	0.90	0.95	0.95
In	0.97	0.89	0.44
Rb	6.37	1.50	1.33
Sb	2.02	1.61	0.51
Se	0.89	0.86	1.21
Te	0.80	1.01	0.60
Tl	—	—	0.74
Zn	0.99	1.03	0.99

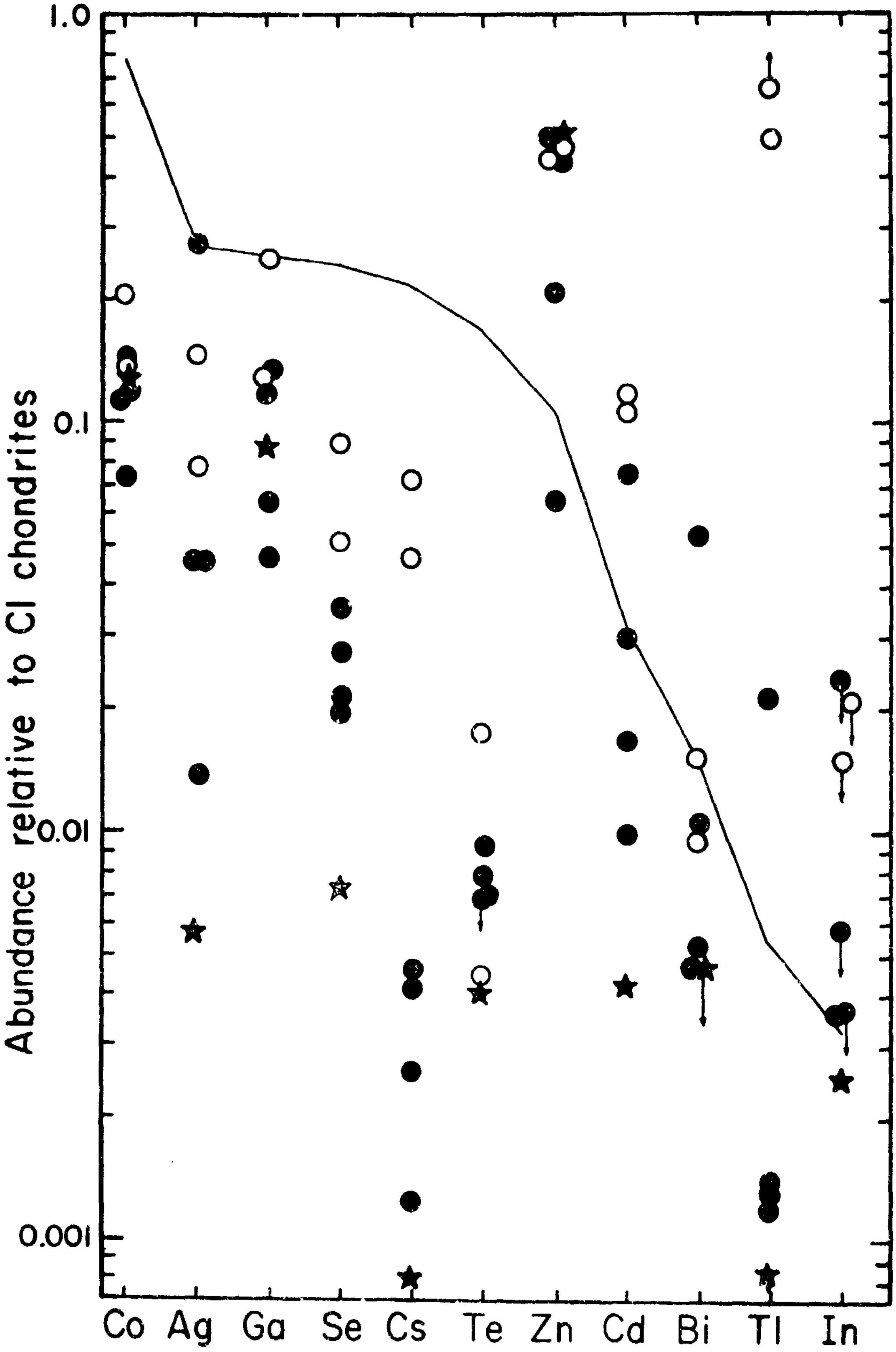
Note to Table 2.

*Values in italics indicate possible weathering effects.

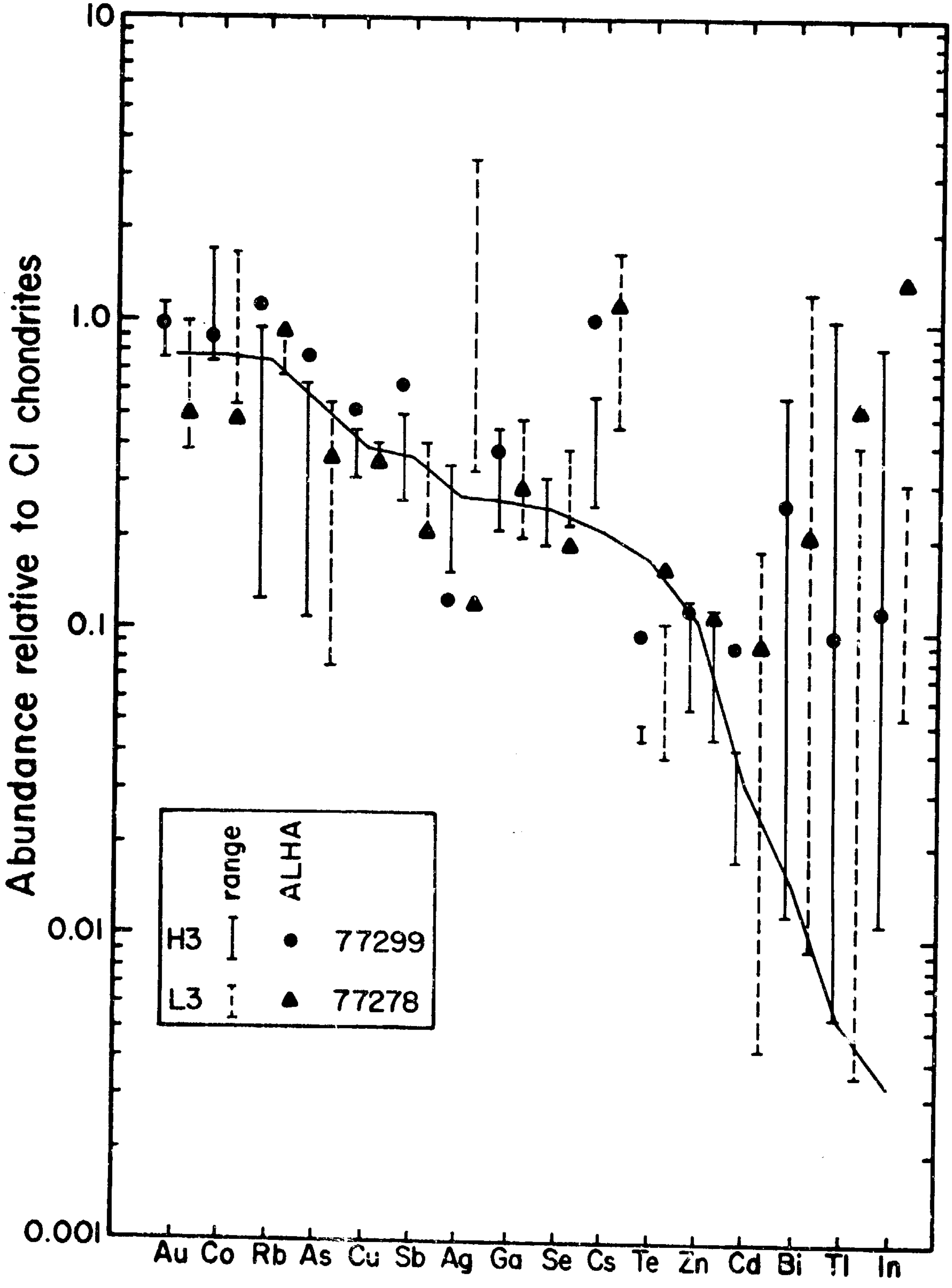
FIGURE CAPTIONS

Figure 1. Depletion factors (i.e. Si-normalized atomic abundances relative to those in Cl chondrites) for ureilites: closed and open circles - falls and finds, respectively; stars - ALHA 77257, 32. Elements are listed from left to right in hypothesized order of nebular volatility as determined from mean depletion factors for equilibrated ordinary chondrites, i.e. the solid more-or-less diagonal line [4,5]. Data for many elements lie below the previously - known range for ureilite falls; the expanded ranges should now be accepted as representative of the ureilite population.

Figure 2. Depletion factors for interior samples - i.e. ALHA 77299, 22 and 77278, 20 - compared with corresponding ranges for all known H3 and L3 chondrites, respectively and with mean depletion factors for equilibrated ordinary chondrites. In most cases, data for Antarctic samples lie within ranges for other type 3 chondrites. Highly-volatile / mobile Cd, Bi, Tl and In in both are clearly enriched relative to equilibrated chondrites, especially in 77278 (see text). Ranges for previously-known H3 and L3 chondrites should be expanded to include the Antarctic samples.



1.0
0.1
0.01
0.001
Abundance relative to CI chondrites
Co Ag Ga Se Cs Te Zn Cd Bi Tl In


Abundance relative to CI chondrites
10
1.0
0.1
0.01
0.001
Au Co Rb As Cu Sb Ag Ga Se Cs Te Zn Cd Bi Tl In
range
ALHA
H3
77299
L3
77278