Trace Element Contents of Selected Antarctic Meteorites. I. Weathering Effects and ALH A77005, A77257, A77278 and A77299

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Dedicated to Professor H. Hintenberger on the occasion of his 70th birthday

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 from the Allan Hills (ALH): A77005 (unique achondrite); A77257 (ureilite); A77278 (L3); A77299 (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 A77005 achondrite seems related to shergottites; other samples extend compositional ranges previously known for their groups or 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; 1.5×10^6 years was determined in one case by Fireman et al. [1] (cf. Evans and Rancitelli [2], Melcher [3]). Many of these stones 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, perhaps less likely on an ice or snow field, enrichment by contamination, we chose to study both siderophile- and volatile-rich (H3, L3) and siderophile- and volatile-poor (ureilite and, as it happens, shergottite-related) meteorites, thus providing material suitable for observing both effects. We determined 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 — e. g. Au, Co, Zn — are extraordinarily resistant to weathering while others — e. g. Ag, Cs, In — seem strongly affected (e. g. Binz et al. [5, 7, 17).

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: A77005, 23 (unique achondrite) -1 cm; A77257, 17 (ureilite) - 0 cm, 29-1 cm, 32-2 cm; A77278, 18 (L3) -0 cm, 20-4 cm; A77299, 22 (H3) -3 cm. We analyzed A77005, 23 and A77278, 20 in duplicate; each sample analyzed was ~ 0.2 g. For reference, dimensions of the whole rocks reported by the MWG are: A77005,

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Table 1. Trace element con-

Meteorite	Type	Ag (ppb)	As (ppb)	Au (ppb)	Bi (ppb)	Cd (ppb)	Co (ppm)	Cs (ppb)
ALH A77005	Achondrite							
,23	interior	3.89	1.33	0.292	—	5.87	65.3	38.0
		4.85	1.41	0.284	0.32	5.92	69.0	38.6
	mean *	4.37	1.37	0.288	≦ 0.72	5.97	67.2	38.3
		± 0.68	**±0.21**	**± 0.007**		**± 0.58**	± 2.6	**± 1.4**
ALH A77257	Ureilite							
,17	exterior	2.14	236	20.1	≦ 0.9	20.8	109	0.78
,29	mid-portion	1.85	206	20.6	≦ 0.9	4.5	83.4	0.34
,32	interior	1.92	273	20.4	≦ 0.9	4.9	109	0.29
ALH A77278	L3							
,18	exterior	33.5	1280	124	32.7	104	467	648
,20	interior	40.5	1220	127	—	106	425	402
		38.9	1150	—	39.8	94.8	422	407
	mean *	39.7	1190	127	39.8	100	424	405
		± 1.6	**± 180**	**± 3**	**± 0.6**	**± 8**	**± 15**	**± 15**
ALH A77299	H3							
,22	interior	38.2	2340	230	45.9	91.2	716	319

* 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: bold-face indicate cases where values for Allende exceed those for the Antarctic meteorite itself and uncertainties in normal type denote the opposite.

9.5 × 7.5 × 5.25 cm; A77217, 16 × 11 × 9.5 cm; A77278, 8.0 × .5 × 4.5 cm; A77299, 9.5 × 5.5 × 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 and Lipschutz [9] were quite comparable and indicated no self-shielding effects for the elements considered here. Chemical and counting procedures, summarized in part by Ngo and Lipschutz [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 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 the 511 keV annihilation radiation; we assured radiochemical purity by following 12.7 hour ^{64}Cu decay for five halflives 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 A77005 and A77257 provided by Ehmann and Young [12] and mean group values of 18.7 and 17.1% Si for A77278 and A77299, respectively, as reviewed by Moore [13].

Results and Discussion

The uncertainties included with our results in Table 1 are the larger of those calculated in two alternative ways. About half are estimates derived from previous analyses in our laboratory of Allende standard meteorite reference material [9, 10, 14];

tents of Antarctic meteorites.

Cu (ppm)	Ga (ppm)	In (ppb)	Rb (ppb)	Sb (ppb)	Se (ppm)	Te (ppb)	Tl (ppm)	Zn (ppm)
5.41	6.01	10.1	502	0.87	0.120	0.43	1.94	47.9
5.52	6.13	12.0	750	0.50	0.177	0.46	1.46	50.8
5.46	6.07	11.1	626	0.68	0.149	0.45	1.70	49.4
± **0.10**	±**0.54**	± 1.3	± 175	± 0.26	± 0.040	± **0.05**	±0.34	± 2.0
3.20	1.63	0.35	8.28	10.0	0.228	18.0	≦0.04	269
3.07	1.72	0.32	1.95	7.99	0.222	22.6	≦0.04	282
3.23	1.81	0.36	1.30	4.96	0.257	22.4	≦0.04	273
78.0	5.48	84.4	4560	28.9	7.82	521	89.4	57.6
87.4	5.86	164	3020	66.8	2.22	862	144	55.5
75.0	5.61	215	3860	46.7	10.7	881	112	61.2
81.2	5.74	190	3440	56.8	6.5	872	128	58.4
± 8.8	±**0.51**	± 36	± 590	± **8.6**	± 6.0	±**100**	± 11	± 4.0
110	7.09	49.3	3820	157	—	487	21.8	56.2

they are probably conservatively high because of minor processing changes in these studies. The other half are based upon duplicate analyses of interior parts of A77005 and A77278 which yielded sample variances greater than those 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 A77257 ureilite and A77278 L3 chondrite indicate significant differences between interiors and outer 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 in A77257, 29, e. g. at the 1 cm depth (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 A77278 (L3); in fact, Sb (and possibly Ag) — like Bi, In, Te and Tl — are depleted in the surface of this L3 chondrite. In A77257 ureilite, 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 A77257, 29 ureilite and Se in A77278 (L3) — seem unusually variable, probably reflecting sample heterogeneity.

We attribute surface enrichments of Cs and Rb in A77257 (ureilite) and A77278 (L3) as due to deposition of wind-borne oceanic aerosol. (We would expect other alkali metals and halides to be affected similarly.) Other elemental enhancements on A77257 must reflect another contamination source since these elements are depleted, presumably by leaching, or are unaffected in A77278. Carbon loss in a C3 and two C2 chondrites (respectively, Yamato 693 and 74662 and ALH A77306) has also been attributed to leaching by Gibson et al. [15]. Cronin et al. [16] report that amino acid compositions in ALH A77306 (C2) 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 not necessarily, by leaching loss. Of the six elements affected by weathering of A77257 ureilite, Binz et al. [7] found that Cd, Cs and Se are enriched (with Tl) in ureilite finds. Binz et al. [7] 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 A77278 (L3) is $\geqq 8.8 \times 10^4$ y [3]. Such limits have been determined for only one other meteorite we studied, A77299

(H3), for which $\geqq 3.5\times 10^4$ 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 A77257 (ureilite) and A77278 (L3), it is important to establish whether elemental concentrations in the interiors of Antarctic meteorites are in digenous. Several circumstantial lines of evidence indicate that this is so.

In the unique achondrite A77005, all trace elements correlate extremely well with values for terrestrial ultramafic rocks or shergottites, achondrites seemingly related mineralogically to this meteorite (cf. McSween et al. [18] for a detailed discussion). It is unlikely that these agreements would be simulated or unaffected by weathering.

The elemental atomic abundance ratios in A77257, 32 (derived from Fig. 1) relative to those in Cl chondrites, are illustrated in Figure 1. Also shown are these ratios for other ureilite finds and falls [17] and for equilibrated ordinary chondrites — which, putatively, are a qualitative measure of elemental nebular volatility [4, 5, 20]. Trends in Fig. 1 and in the outer part(s) of A77257 indicate that the principal weathering effect in ureilites is contamination. If interior parts of A77257 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 (Figure 1). Data for the other 8 elements in ALH A77257, 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 A77257, 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 ALH A77278, 20 and A77299, 22 (e. g. interior samples) yield depletion factors lying within corresponding ranges for L3 and H3 chondrites, respectively. For A77299, 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 A77278, 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 A77278 and A77299 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 A77257 and A77278 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 or mean deviation of Fe in ferromagnesian silicates; Bi is also correlated save in the most unequilibrated cases where it is anomalously low [5]. For A77278, In and Tl lie above the known range for L3 chondrites

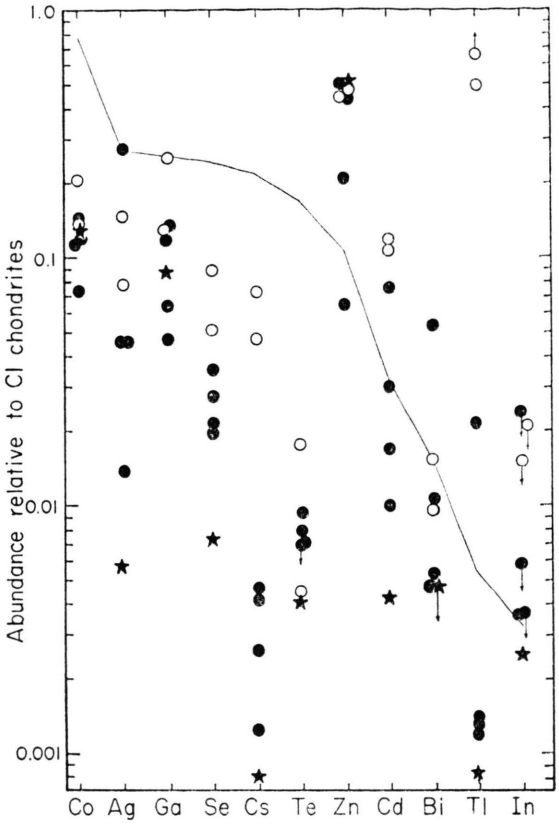

Fig. 1. Depletion factors (i. e. Si-normalized atomic abundances relative to those in Cl chondrites) for ureilites: closed and open circles — falls and finds, respectively; stars — A77257, 32. Elements are listed from left to right in hypothesized order of nebular volatility as determined from mean depletion 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.

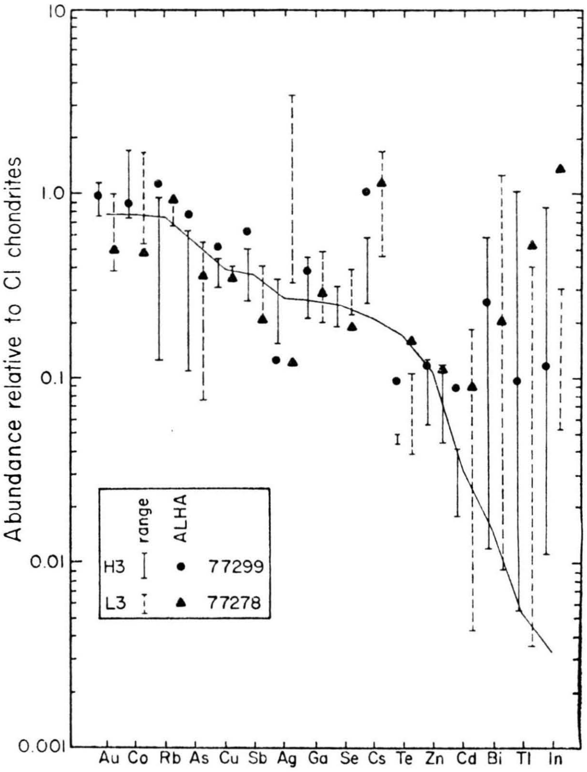

Fig. 2. Depletion factors for interior samples — i. e. A77299, 22 and A77278, 20 — compared with corresponding ranges for all known H3 and L3 chondrites, respectively and with mean depletion factors for equilibrated ordinary chondrites. In most cases, data for Antarctic samples lie within ranges for other type 3 chondrites. Highly-volatile/mobile Cd, Bi, Tl and In in both are clearly enriched relative to equilibrated chondrites, especially in A77278 (see text). Ranges for previously-known H3 and L3 chondrites should be expanded to include the Antarctic samples.

while Bi is well within it but toward the high end (Figure 2). Indeed, In in A77278 exceeds Cl levels; no other known ordinary chondrite is so enriched (Figure 2). ALH A77278 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 all trace elements in A77278.

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 groups or 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 A77005 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.

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

	Interior-normalized contents		
	A77257 *		A77278 *
	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**

* Values in bold-face indicate possible weathering effects.

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